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An Investigation of the Determination of Molecular Weights of High Polymers by Light Scattering

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The determination of the molecular weights of large molecules by measuring the turbidity of the solution and the change in index of refraction with concentration is discussed. The apparatus, its calibration, and the technique used are treated together with a comparison between molecular weights measured by this method and other methods. The effect of polymolecularity is also presented.

INTRODUCTION

RECENTLY Debye[1] has pointed out that the measurement of light scattering in solutions may be used to determine the molecular weights of high polymers. Since that time we have been interested in examining this method and some data of preliminary experiments have already been published.[2] In the continuation of this investigation a few anomalies have been noted which are as yet incompletely understood. However, in view of the apparent success of this method, we report here in more detail concerning the experimental methods used and some further results obtained. Some limitations and pitfalls as well as an extension of the method to the characterization of molecular weight distributions are discussed.

Before proceeding we review briefly the theoretical background.[3,4] It is common knowledge that some light is always scattered from a beam of light passing through a transparent fluid (Tyndall effect). This, however, would not occur in a medium which was perfectly uniform. Real solutions are never perfectly uniform because of minute thermal fluctuations in density and concentration. These inhomogeneities are the source of the scattered light. The extent of the fluctuations is determined by the free energy change (work) necessary to produce them. On the basis of these considerations, von Smoluchowski[5] and Einstein[6] derived the following expression for the turbidity of a colorless binary mixture.

$$\tau_0=\frac{32\pi^3n^2}{3\lambda^4N_0}\times\left\{RT\beta\left(\rho\frac{\partial n}{\partial\rho}\right)^2+\frac{M_1c}{\rho\left(-\dfrac{\partial\ln f_1}{\partial c}\right)}\left(\frac{\partial n}{\partial c}\right)^2\right\}. \quad (1)$$

τ_0, the turbidity of the solution, corresponds to the extinction coefficient in Lambert's law,

[1] P. Debye, J. Appl. Phys. **15**, 456 (1944).
[2] P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. **12**, 144 (1944).
[3] S. Bhagavantam, *The Scattering of Light and Raman Effect* (Anhandra University, Waltair, India, 1940); American Edition (Chemical Publishing Company, Brooklyn, New York, 1942).
[4] J. Cabannes, *La Diffusion Molèculaire de la Lumiére* (Les Presses Universitaires de France, Paris, 1929).
[5] M. von Smoluchowski, Ann. d. Physik **25**, 205 (1908).
[6] A. Einstein, Ann. d. Physik **33**, 1275 (1910).

i.e., it is the fractional decrease in the intensity of incident light upon transversing one centimeter of solution, the decrease occurring only from scattering—not absorption. The other symbols are: λ = wave-length in vacuum (cm^{-1}); N_0 = Avogadro's number; R = molar gas constant; T = temperature (°K); β = isothermal compressibility; ρ = density; n = refractive index of solution; M_1 = molecular weight of solvent; f_1 = fugacity of solvent; and c = concentration of solute in grams per cm^3 of solution.

While Eq. (1) has been used successfully in this and previous investigations in this laboratory, and is essentially the one used by Debye,[1] it should be remarked that there is not unanimous agreement on the value of the constant factor before the braces in Eq. (1). Several authors have proposed the introduction of a factor $[(n^2+2)/3]^2$ in this constant. The arguments are well summarized by Cabannes.[4] Since previous experiments[4] designed to decide the question (by measurement of the light scattered by one-component liquids) have apparently been inconclusive, we have not yet attempted to decide the question but have used the formula as originally proposed.

The first term in Eq. (1) represents the turbidity arising from fluctuations of density. This part of τ_0 corresponds essentially to the turbidity of the pure solvent (assuming β to be constant). Thus if the measured turbidity of the solvent is subtracted from τ_0 the remainder, τ, represents the turbidity caused by concentration fluctuations, a quantity directly related to the solute molecular weight.

Substituting in (1) the thermodynamic relation

$$-\partial \ln f_1/\partial c = (\bar{V}_1/RT)(\partial\pi/\partial c), \qquad (2)$$

there is obtained (2)

$$\tau = \frac{32\pi^3 c n^2 (\partial n/\partial c)^2}{3\lambda^4 N_0 (1/RT)(\partial\pi/\partial c)}, \qquad (3)$$

where π is the osmotic pressure and $\bar{V}_1$ the partial molal volume of the solvent has been replaced by its approximate equivalent M_1/ρ. The osmotic pressure of high-polymer solution of low concentration is given by

$$\pi = (RT/M_2)c + Bc^2 + \cdots, \qquad (4)$$

which, when substituted into (3), gives upon rearrangement

$$\frac{c}{\tau} = \frac{3\lambda^4 N_0}{32\pi^3 n^2 (\partial n/\partial c)^2}\left[\frac{1}{M_2} + \frac{2B}{RT}c + \cdots\right] = \frac{1}{H}\left[\frac{1}{M_2} + \frac{2B}{RT}c + \cdots\right]. \qquad (5)$$

Thus it appears that a plot of Hc/τ *versus* c should give at low concentration a straight line whose intercept is the reciprocal of the molecular weight of the solute. Furthermore, the slope of this plot is twice the slope obtained from osmotic pressure measurements when π/cRT is plotted against c. In this way the measurement of the two optical quantities, (1) turbidity as a function of concentration and (2) the change of index of refraction with concentration, gives information similar to that obtained from direct osmotic pressure measurements.

However, it is important to note that whereas osmotic pressure measurements yield a number average molecular weight, turbidity measurements yield a weight average.* In the final section a more exact discussion of this point occurs, but the conclusion can be seen intuitively from a molecular picture of light scattering. In a *very* dilute solution the intensity of the scattered light is equal to the sum of the intensities of the light scattered by the individual molecules.[1] The intensity of the light scattered by a single molecule of a given species is proportional to the square of the molecular weight. Since the number of molecules is equal to the total weight of that

TABLE I. Comparison of molecular weight measurement.

Material	Molecular weight: Osmotic pressure	Molecular weight: Light scattering
Polystyrene, No. 1	172,000	178,000*
Polystyrene, No. 2	198,000	182,000
Polystyrene, No. 3	91,000	107,000
Polystyrene, No. 4	—	190,000
Polystyrene, No. 5	—	445,000
Cellulose Acetate, No. 1	(125,000)	123,000
Cellulose Acetate, No. 3	75,000	76,000

* This value was checked independently by two other laboratories.

* The number average molecular weight ($\Sigma M_i N_i/\Sigma N_i$) counts each molecule with equal weight, whereas the weight average ($\Sigma M_i^2 N_i/\Sigma M_i N_i$) weights each molecule according to its mass.

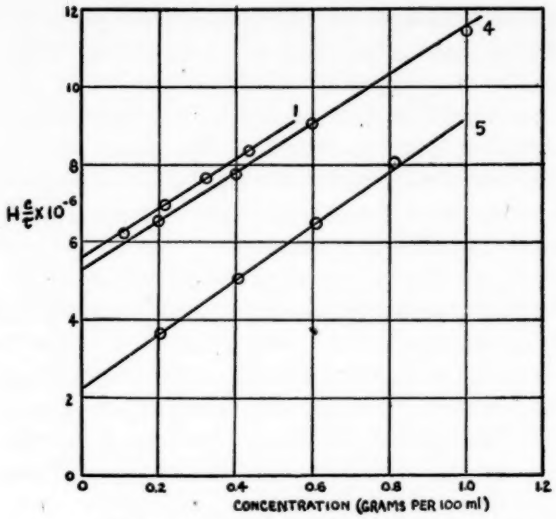

FIG. 1. Plot of turbidity data for polystyrene fractions in methyl ethyl ketone.

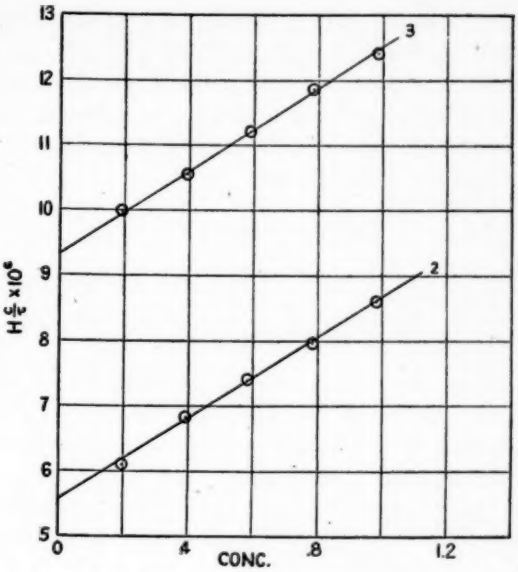

FIG. 2. Plot of turbidity data for polystyrene fractions in methyl ethyl ketone.

species divided by the weight of the individual molecule, the total intensity of light scattered from one species is therefore proportional to the weight of that species multiplied by its molecular weight. Averaging over all molecular weight species yields the weight average molecular weight. This conclusion has been experimentally demonstrated.[7]

EXPERIMENTAL DETAILS

Numerous methods may be adapted to measure the turbidity of high-polymer solutions. One could hope to measure τ directly by measuring the transmission of the solutions. This is usually unsatisfactory, however, because of the small values of τ (10^{-2} to 10^{-4} cm^{-1}) and the frequent presence of absorbing impurities. On the other hand, direct measurement of the intensity of the scattered light conveniently avoids these difficulties and readily lends itself to visual or photoelectric observation. Moreover, it has been our observation that transmission measurements are subject to a number of uncertainties, the absence of which can be assured only by measurements over a rather large spectral range. True absorption, low angle scattering, small amounts of impurities, solute size comparable with wavelength, and other effects still not understood, may prevent the turbidity as measured by transmission from being the proper value to use in Eq. (5).

Although photoelectric methods are always capable of greater precision, the visual method has certain inherent advantages, such as small aperture, direct view of scattering solution, exact linearity, and freedom from electrical difficulties. We have constructed a turbidimeter attachment** for use with the Zeiss Pulfrich photometer. This turbidimeter was patterned after the Zeiss turbidimeter, except that the light scattered is observed at an angle of 90° to the incident beam, instead of 135°. Light from a mercury bulb (AH-4 100 watt G.E.) is rendered parallel by lens and passes through the solution in a square cell. A small, constant fraction of the incident light is reflected from a glass plate (mounted in the beam) to an opalescent glass which serves as a standard comparison source for the photometer. The dial reading corresponding to matched fields in the photometer is directly proportional to the total turbidity.

It is necessary to calibrate the instrument; that is, to determine the proportionality constant between dial reading and absolute turbidity. One method of calibration is based on measuring the ratio of the intensities of the incident and

[7] B. H. Zimm and P. M. Doty, J. Chem. Phys. 12, 203 (1944).

** General Gauge and Tool Company, 30 Irving Place, New York.

scattered light, with the help of a white (magnesium carbonate) surface making a 45° angle with the incident beam in place of the solutions. If the solution and the magnesium carbonate are measured successively, the ratio of the photometer readings gives the quantity

$$(ir^2/I)(h\pi/\sin 45°),$$

where i is the intensity of the light scattered from one cubic centimeter of solution at distance r, I is the intensity of the incident beam, and h is the width (in the direction of observation) of the incident beam of homogeneous density. If the scattering of the solutions obeys Rayleigh's law for its angular distribution, i.e., if it varies as $(1+\cos^2\theta)$ where θ is the angle between incident beam and direction of observation, integration gives

$$\tau_0=(16\pi/3)(ir^2/I).$$

Correction must be made for the reflectivity of magnesium carbonate (97.5 percent) and for reflection at the glass-air interfaces. Thus the calibration consists of the determination of the ratio of the photometer readings with solution and block in the cell successively together with the measurement of the width of the incident beam in the cell.

Another means of calibration is based on the use of standard opalescent glass prisms furnished by Carl Zeiss and Company. A polymer solution was measured in a Zeiss turbidimeter using two of these standard prisms. The value of the turbidity so obtained checked satisfactorily the turbidity found for the same solution by the previous method.

The measurement of the transmission of a strongly scattering colorless solution offers another method of determining absolute turbidity. Several preliminary attempts yielded inconsistent turbidity values that were also too large, probably indicating absorption. The investigation of this method is continuing.

The sensitivity of our instrument is such that τ_0 values as small as 10^{-4} cm^{-1} may be measured with a reproducibility of 2 percent.

The other optical measurement necessary is the evaluation of $\partial n/\partial c$. Our measurements have confirmed that n varies linearly with c at low concentrations. Consequently one measurement of the refractive index difference between the solvent and solution determines $\partial n/\partial c$. Since usually the magnitude of the difference for a 1 percent solution is approximately 0.001, a differential method is desirable. We have used a Pulfrich refractometer with a divided cell for this purpose, thus permitting a precision of about 1 percent in this measurement.

Depolarization (ratio of the intensities of the horizontal to vertical components in the scattered light) can easily be measured by the use of a Polaroid or nicol inserted in the solution side of the photometer. Strictly speaking, Eqs. (1) and (5) should contain a factor (Cabannes), depending on the depolarization, which arises from fluctuations in orientation of anisotropic molecules.[1,3,4] In the work reported here the depolarization was so small that this factor was essentially unity.

All solutions and solvents were filtered through fine or medium sintered glass filters. A deep glass cell (3×3×10 cm) has been used in later work. This permits one to begin measurements with 25 cc of (say) a 1 percent solution. Measured amounts of filtered solvent may be added and stirred; thus all the measurements at different concentrations are made in one continuous operation.

RESULTS

In this section typical examples of the use of this method on some fractionated high polymers are presented together with available osmotic pressure data. The results of the turbidity measurements and osmotic pressure measurements are shown in Table I for the fractions studied.

The most carefully measured fraction (No. 1) was one prepared and measured osmotically by Hanson.[8] The other two polystyrene fractions (Nos. 2 and 3) were prepared and their osmotic pressure determined in this laboratory several years ago. In Figs. 1 and 2 the turbidity data are plotted in such a manner that the intercept is the reciprocal of the molecular weight. The data for two other fractions for which no other molecular weight data are available are also shown in Fig. 1.

The need for extrapolation of $H(c/\tau)$ to infinite

[8] J. Hanson, Thesis, Polytechnic Institute of Brooklyn, 1944.

dilution is clearly shown in the figures. For example, if the molecular weight of sample No. 5 were calculated from the turbidity of its 1 percent solution alone, the value would have been 110,000, instead of the actual value of 445,000. The higher the molecular weight, the larger the error which results from use of data without extrapolation.

The cellulose acetate fractions were prepared by Badgley.[9] The molecular weight in parenthesis is from viscosity measurements. However, the viscosity-molecular weight equation for this series of fractions has been so well established[9] that the value has the validity of an osmotic pressure measurement.

It is interesting to examine the relation between the slope of the $H(c/\tau)$ *versus* c plot and the π/c *versus* c plot. As stated previously, if osmotic pressure is represented by

$$\pi=(RT/M_2)c+Bc^2, \tag{4}$$

the slope of the turbidity graphs should give the value of $2B/RT$.

If one uses Huggins' equation[10]

$$\frac{\pi}{c}=\frac{RT}{M_2}+\frac{RT}{V_1 d_2{}^2}(\tfrac{1}{2}-\mu_1)c, \tag{6}$$

where V_1 is the molar volume of solvent, d_2 is the density of solute, μ, the empirical constant of the solvent-solute system, may be used to characterize the slope, B, of the π/c *versus* c plots. That is:

$$\frac{\Delta(\pi/c)}{\Delta c}=\frac{RT}{V_1 d_2{}^2}(\tfrac{1}{2}-\mu_1),$$

and

$$\frac{\Delta[H(c/\tau)]}{\Delta c}=\frac{2}{V_1 d_2{}^2}(\tfrac{1}{2}-\mu_1). \tag{7}$$

In other words, it is convenient to compare the slopes of the lines obtained from plots of osmotic pressure and turbidity data by calculating the μ_1, from Eq. (7). In Table II the μ_1 values of the polystyrene-toluene system (previously reported) and cellulose acetate-acetone system obtained from turbidity data are compared with μ_1 calculated from osmotic pressure measurements on the same system.

TABLE II. Comparison of μ values.

	μ (Osmotic pressure)	μ (Light scattering)
Polystyrene-toluene	0.43–0.45[a,b] 0.44[d]	0.43–0.44[c]
Polystyrene—MEK	—	0.47–0.48*
Cellulose acetate-acetone	0.42–0.43[e]	0.44*

* This research.
[a] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943).
[b] Reference 8.
[c] Reference 2.
[d] G. V. Schultz, Zeits. f. physik. Chemie **A176**, 317 (1936).
[e] Reference 9.

DISCUSSION

When the particle size of the solute becomes comparable to the wave-length of light, interference between waves from different parts of the same particle occurs and the simple theory outlined above breaks down. The total scattered intensity then falls below that given by Eq. (5). At the same time, instead of the angular distribution of the scattered light being symmetrical about 90° (as is the case with small particles), interference in the case of large particles causes more light to be scattered in the forward than in the backward direction. Measurement of the symmetry of the scattered intensity therefore furnishes a test of the applicability of Eq. (5).

For spherical particles, deviations from Eq. (5) become noticeable when the particle diameter exceeds about one-tenth the wave-length of light. Polymer chain lengths frequently are greater than this by a large margin so that it might be expected that interference would often occur. However, most high-polymer molecules are believed to be loosely convoluted in solution so that the longest dimension of the molecule is on the average much less than the chain length. It is clear that this point is critical, for the average extension of a *randomly* coiled polymer molecule of moderate weight will not exceed one-tenth the wave-length of light, whereas the common interpretation of viscosity measurements, sedimentation constants, and flow birefringence indicate that most polymer molecules are more extended in solution and hence should give rise to a dissymmetry of the angular intensity of the scattered light.

A simple instrument has been constructed to

[9] W. Badgley, Thesis, Polytechnic Institute of Brooklyn, 1945.
[10] M. L. Huggins, Ann. N. Y. Acad. Sci. **41**, 1 (1942).

measure the dissymmetry. A parallel beam of monochromatic light is passed through the solution in a five sided cell. The light scattered at 45° on each side of the normal plane is reflected by the mirrors to the photometer apertures. The relative intensities are then compared by means of the photometer.

Measurements of this type on the solutions of polystyrene in methyl ethyl ketone showed practically no dissymmetry, thus permitting the direct application of Eq. (5). Incidentally the higher molecular weight polystyrene fraction No. 5, dissolved in toluene did exhibit a considerable dissymmetry indicating that the molecule is more extended in the better solvent. On the other hand, all of the cellulose acetates reported here gave noticeable dissymmetries in acetone solution. Corrections based on these measured dissymmetries range upward to 20 percent and have been applied to the results listed in Table II. A detailed discussion of these measurements and corrections will be given later when this study of cellulose acetate fractions is finished.

In most cases, solutions in the concentration range between 1.0 gram and 10.0 grams of polymer per liter have been used both for turbidity and refractive index measurements. The polymer specimens were the result of repeated fractionation of a commercial material or of a sample polymerized under certain controlled conditions. Two types of impurities, which can never be completely eliminated, require special attention and care:

A. Low molecular weight impurities of the solvent or the polymer. All solvents were carefully distilled until their characteristics, such as density, boiling point, and refractive index, did not undergo any changes upon further purification. Some solvents, such as dioxane, formic acid, etc. retain water very tenaciously and have to be kept carefully dry, because even small amounts of water affect the refractive index noticeably. The polymers should be dissolved and reprecipitated before they can be brought into the solution which is finally used for the measurements. It seems advisable to prepare a 2–3 percent solution of the original polymer in the same solvent in which the final measurements are contemplated, and to precipitate it with a volatile precipitant. The precipitate is filtered off and thoroughly washed with the precipitant. It is then slowly dried at low temperatures in vacuum. Fast drying under more vigorous conditions, such as elevated temperature, leads in certain cases to hornification of the samples, which makes subsequent dissolving difficult and eventually even leads to solutions containing minute gel particles, which may lead to excessive scattering. This process of purification through precipitation should be repeated one or more times; some polymers, e.g., polystyrene, are relatively easily separated from traces of monomer, catalysts, or stabilizers, others e.g., Nylon or rubbery copolymers, retain impurities rather tenaciously. It does not seem easy to prepare any strict prescription at present, and it will be necessary to collect further experience until certain standard procedures can be recommended.

B. Coarse impurities of the solvent and polymer. All solvents and solutions have to be filtered repeatedly until they appear optically clean and until further filtration does not decrease the turbidity any more. All solvents contain a certain amount of dust of mostly inorganic origin, which can be satisfactorily reduced to an insignificant amount by repeated filtration through glass fritters. All polymers contain coarse impurities of various types. Dust of inorganic origin, having large particle sizes (several microns), is comparatively easily removed by precipitation, washing, redissolution, and final filtration through glass fritters. Haze, of organic origin, is frequently owing to chemical and structural heterogeneity of the polymer, such as too highly (or too lowly) acetylated fractions in cellulose acetate or branched (even cross-linked) constituents in vinyl polymers and copolymers. This type of haze, which is chemically closely related to the investigated material and differs from it only slightly in its solubility characteristics, sometimes offers very serious obstacles and eventually can prevent the application of the light scattering method altogether. It seems that a comparatively successful way to reduce this haze is to precipitate the polymer three or four times, using each time *another* solvent and eventually also more than one precipitant. It can be directly observed in such cases that the turbidity of the solution decreases visibly after

each precipitation, but even a solution which appears completely transparent to the eye may still contain enough haze particles to give wrong results. These very large complexes affect the light scattering in about the same way as they affect specific viscosity, because of the fact that they contribute to the total effect according to their weight. Their large size (1000A or more), on the other hand, makes it possible to obtain independent experimental evidence about their presence by measuring the dependence of the turbidity upon the angle between incident and scattered light in the apparatus described previously.

In choosing a solvent for this type of work, one must be mindful of the great importance of the difference in index of refraction between solvent and solute. This difference should be greater than 0.0005 refractive index unit between a 1 percent solution and the solvent. In fact, it is just this difference which determines the lowest molecular weight which can be measured with a given accuracy, for, obviously, the greater the refractive index difference, the lower the molecular weight solute that will give the same scattering. The lowest molecular weights we have measured were near 10,000 where $\partial n/\partial c = 0.07$ for the system investigated. To measure molecular weights lower than this $\partial n/\partial c$ would have to be increased by use of a different solvent or less accuracy would have to be expected. Thus at present the method is limited to molecular weights above 10,000.

Colored solutions offer some difficulty; however, by using light of a wave-length that is outside the absorption band of the solution no trouble is encountered.

At the end of this section it may be reiterated that the few recommendations made are far from being a well worked-out technique. They only represent the limited experience collected during a short period and will have to be considerably improved and expanded in the future.

MOLECULAR WEIGHT DISTRIBUTION

It was shown in a previous letter by Zimm and Doty[7] that Eq. (5) can be generalized to include the case of a solute containing molecules of different degrees of polymerization. By the same methods used to derive Eq. (1), the turbidity of a solution of several different solutes in the same solvent can be shown to be

$$\tau = \frac{32\pi^3 M_1 n^2}{3N_0\lambda^4\rho} \sum_i \frac{(\partial n/\partial c_i)^2 c_i}{(-\partial \ln f_1/\partial c_i)}, \qquad (8)$$

where c_i is the concentration (g/cc) of the ith species of solute.

If all the solute species are homologous polymers of the same monomer, differing only in molecular weight, two important simplifications can be made. In the first place, one might reasonably expect $\partial n/\partial c$ to be independent of the molecular weight so that it can be factored out of the sum. In the second place, it is generally known that the coefficient of the second term in the expansion of the osmotic pressure in terms of concentration (Eq. (1)) is independent of molecular weight in a homologous polymeric series. We might expect, therefore, that this coefficient would be constant in a solution of mixed homologs as in the following equation

$$\pi = \sum \frac{RT}{M_i} c_i + Bc^2 + Cc^3 + \cdots, \qquad (9)$$

where B is independent of molecular weight.

Introduction of these assumptions leads[7] to the following expansion for $H(c/\tau)$

$$H\left(\frac{c}{\tau}\right) = \frac{1}{\bar{M}} + \frac{2B}{RT}\left[1 + \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right]c + \left\{\frac{3C}{RT}\left[1 + \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right] + \frac{4B^2\bar{M}}{R^2T^2}\left[\left\{\left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av}\right\}^2 - \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^2\right\rangle_{Av} - \left\langle\left(\frac{\Delta M}{\bar{M}}\right)^3\right\rangle_{Av}\right]\right\}c^2 + \cdots, \qquad (10)$$

where $\bar{M}$ is the weight average molecular weight and $\langle(\Delta M/\bar{M})^2\rangle_{Av}$ and $\langle(\Delta M/\bar{M})^3\rangle_{Av}$ are the second and third moments of the molecular weight distribution curves about the weight average molecular weight. This reduces to Eq. (5) when the moments are all zero, i.e., when the solute consists of one molecular weight species only.

It can immediately be seen that the plot of $H(c/\tau)$ for solutions of mixed molecular weight may have appreciable (downward) curvature.

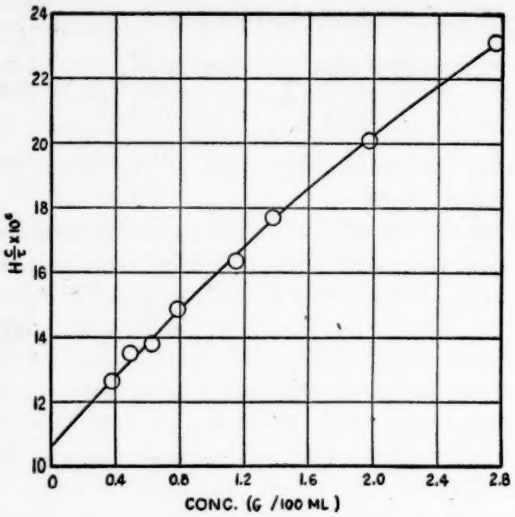

FIG. 3. Turbidity measurements on cellulose acetate in acetone.

Experimental data on a solution of unfractionated cellulose acetate shown in Fig. 3 illustrate this predicted curvature. We see here an observable effect of non-homogeneity of molecular weight which has no counterpart in the case of osmotic pressure. This difference arises from the same reasons that cause osmotic pressure to be related to number average and turbidity to weight average molecular weight.

One way of utilizing this difference would be to plot $H(c/\tau)$ *versus* c for the unfractionated polymer and draw the best curve through the data. Then either from turbidity measurements on a fraction or from osmotic pressure measurements on the unfractionated polymer one may obtain the slope of the $H(c/\tau)$ *versus* c plot for a fraction. The difference between this slope and the initial slope of $H(c/\tau)$ *versus* c for the unfractionated polymer will give the value of the second moment,

$$\langle(\Delta M/\bar{M})^2\rangle_{Av},$$

which characterizes the "width" of the distribution curve or the dispersion of molecular weights about the average value. By ordinary curve fitting methods the coefficient of the c^2 in Eq. (10) may be determined, from which the third moment,

$$\langle(\Delta M/\bar{M})^3\rangle_{Av},$$

may be evaluated using the previously found value for the second moment. This third moment characterizes the asymmetry of the molecular weight distribution curve. The determination of higher moments would lead to more specific information about the distribution curve but at present this seems impracticable both experimentally and theoretically, for extremely accurate measurements would be required and the compliance of Eq. (10) with the system investigated would have to be rigorously proven. A study of the application of this general method is being continued.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Professor Debye, P. P. Debye, and F. W. Billmeyer for many interesting and helpful discussions with them relating to this work and for the opportunity to inspect the equipment at Cornell University before beginning experiments here. The assistance of Mr. Irving Meyerson and Mr. R. Stein in some of the experimental work is greatly appreciated. We are indebted to Professor C. O. Beckmann of Columbia University for use of some optical equipment.

The Near Ultraviolet Absorption Spectrum of Aniline Vapor

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The absorption spectrum of aniline vapor has been photographed in the first and second order of a 3-m grating spectrograph. The strongest bands appeared as doublets and on the basis of these, a tentative analysis was made and compared with the available Raman data.

INTRODUCTION

THE analysis of the near ultraviolet absorption spectrum of benzene[1] has shown that only the transitions involving non-totally symmetric vibrations of the ϵ_g^+ type are allowed. It has been further shown[2] that a modification of the electronic structure by substitution tends to remove the restriction so as to allow the 0−0 transition and transitions not involving the ϵ_g^+ type of vibration. The modification of the electronic structure of the benzene nucleus occurs by virtue of an inductive effect which is dependent on the electronegativity of the substituent and a resonance effect which requires an unshared pair of electrons on the substituent.

Sponer and Wollman[3] have shown the presence of two spectra, in monochlorobenzene one involving an ϵ_g^+ vibration and other involving symmetric vibrations only, in addition to the 0−0 transition. It was expected that the aniline spectrum would show the same features with the symmetrical frequencies appearing more strongly because the electronegativity of the NH_2 group is lower than that of chlorine.

Aniline has been previously studied by several different investigators in the ultraviolet,[4] in the infra-red,[5] and by means of the Raman effect.[6]

EXPERIMENTAL

The spectrum of aniline, which lies in the region of 2500–3000A, (Fig. 1) was photographed in both the first and second orders of a spectrograph of the Eagle type, using a 3-m grating ruled 15,000 lines per inch. The light source was a 5000-volt, 2.5-kva hydrogen discharge tube constructed by the Hanovia Chemical Company. The plates used were Eastman Kodak 103-0 and 103-0 uv-sensitive, the exposure times varying between ten minutes and two hours. The comparison spectrum of iron was obtained from a standard arc of the Pfund type. The absorption cell was all quartz, 70 cm long, connected to a reservoir containing the aniline. After evacuation of the cell, the aniline pressure was controlled by fixing the temperature of the reservoir. Plates were taken with temperatures ranging between −20°C and 25°C, the cell in every case being at room temperature.

After each run it was necessary to carefully clean the absorption cell due to photodecomposition which deposited a film on the windows. The film seemed to have a continuous absorption and so did not interfere with the development of the spectrum, but did necessitate longer exposures if allowed to build up to any appreciable thickness. No detectable differences were found between short first-order exposures and the longer second-order ones indicating that the photodecomposition products did not seriously interfere.

The aniline used in this investigation was the Eastman Kodak "white label" grade which was

[1] H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys. **7**, 207 (1939).
[2] A. L. Sklar, J. Chem. Phys. **7**, 984 (1939).
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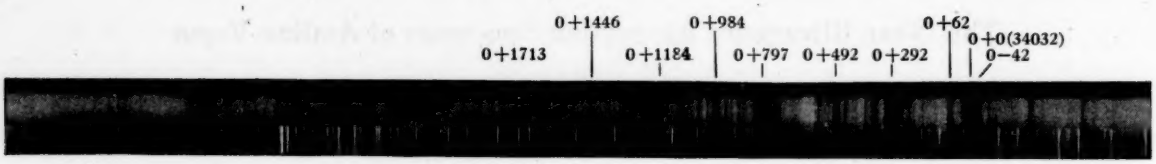

FIG. 1. The absorption spectrum of aniline vapor. (Negative print.)

redistilled in a meter-long, packed, adiabatic column just before use, the middle third of the distillate being kept for this investigation. Its boiling point was found to be 173.1°C at 750 mm.

The plates were measured on a Gaertner comparator, and on reduction the results from both orders were found to be in good agreement. The wave-lengths as given in Table I are the average of three second-order plates. Almost all of the stronger lines appeared as close, well-resolved doublets (Fig. 2) and because these were very sharp with no apparent degradation, the center of gravity of each of the components was measured. This method was also applied to those bands which did not appear as doublets. The precision varied from 0.3 cm^{-1} for the sharp doublets to 2 or 3 cm^{-1} for the weaker, more diffuse bands.

DISCUSSION

Over 500 bands were observed in a frequency range of just over 6000 cm^{-1}. In the central region of the absorption spectrum the average separation of the bands was about 8 cm^{-1}. Since with this separation, it was impossible to make an unique assignment, and since the doublet spectrum mentioned above stood out on the basis of intensity and character, an analysis was made of this spectrum only.[7]

From the observed frequencies of the lines, a difference table was prepared and the appearance number of the prominent differences noted. Several of the strongest bands were separated from the 0−0 band by frequencies which had high appearance numbers in the difference table. These frequencies were then taken as the vibrational frequencies for the excited state, and the assignment of the remaining doublets made on that basis (Tables I and II).

The first strong doublet and the most intense of all is the one at 34,032–34,035. Following Sponer and Wollman, the lower frequency component was chosen as the 0−0 line despite the fact that there was no difference in intensity

[7] Sponer and Wollman have observed similar doublets in chlorobenzene. Benzene also shows this doublet structure. The doublet separation of 3 cm^{-1} is of the right order of magnitude to be attributed to rotational structure.

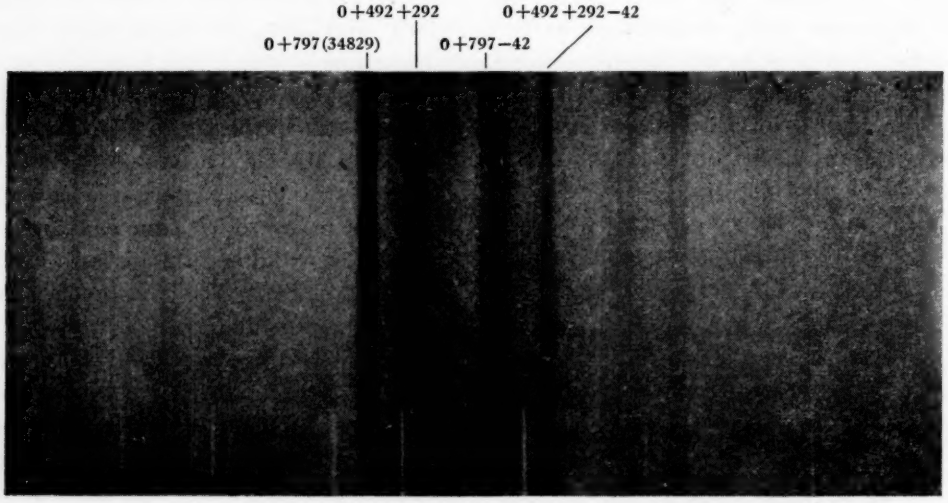

FIG. 2. The fine structure of aniline absorption bands in the region of 34,800 cm^{-1}. (Negative print×4.)

TABLE I. The spectrum of aniline. The intensities are designated as *vw* = very weak, *w* = weak, *m* = medium, *ms* = medium strong, *s* = strong, *vs* = very strong, and *vvs* = extremely strong, *B* = broad and *D* = diffuse.

Frequency (cm^{-1})	Intensity	Assignment
A. The Double Bands		
33,376	*w*	0−231−423
33,381	*w*	
33,501	*mB*	0−531
33,506	*mB*	
33,569	*m*	0−423−42
33,573	*m*	
33,609.1	*vs*	0−423
33,612	*vs*	
33,754	*m*	
33,757	*m*	
33,801	*s*	0−231
33,804	*ms*	
33,908	*m*	0−3×42
33,912	*m*	
33,948	*ms*	0−2×42
33,950.9	*ms*	
33,980	*ms*	
33,982	*ms*	
33,991	*vs*	0−42 (953−994)
33,994	*vs*	
34,032	*vvs*	0−0
34,035	*vvs*	
34,094	*ms*	0+62 (292−231)
34,097	*s*	
34,193	*m*	
34,197	*m*	
34,205	*m*	
34,208	*m*	
34,241	*ms*	0+292−2×42
34,244	*ms*	
34,283	*vvs*	0+292−42
34,286	*vvs*	
34,297	*s*	0+797−531
34,299	*s*	
34,314	*vs*	0+282
34,317	*vs*	
34,324	*vvs*	0+292
34,326	*vvs*	
34,369.6	*ms*	0+338
34,373.7	*ms*	
34,406	*vs*	0+797−423
34,409	*vs*	
34,440	*ms*	0+492−2×42
34,443	*ms*	
34,483	*vs*	0+492−42
34,486	*vs*	
34,512	*msD*	
34,515	*msD*	
34,524	*vvs*	0+492
34,527	*vvs*	
34,563	*m*	0+953−423
34,566	*m*	
34,586	*vs*	0+492+62
34,590	*vs*	
34,599	*w*	0+567
34,602	*w*	
34,707	*m*	0+717−42
34,709.4	*m*	
A. The Double Bands		
34,733	*s*	0+492+292
34,736	*s*	−2×42
34,749.2	*s*	0+717
34,753	*s*	
34,774	*vs*	0+492+292−42
34,777	*vs*	
34,788	*vs*	0+797−42
34,792	*vs*	
34,805	*ms*	0+492+282
34,809	*ms*	
34,814	*vvs*	0+492+292
34,817	*vvs*	
34,829	*vs*	0+797
34,833	*vs*	
34,861	*m*	0+492+338
34,866	*m*	
34,891.1	*ms*	0+797+62,
34,895		0+292+567
34,923	*ms*	0+492+338+62
34,926	*ms*	
34,943	*s*	0+953−42
34,945	*s*	
34,975	*sD*	0+2×492−42
34,978	*sD*	
34,985	*s*	0+953
34,988	*s*	
34,992	*s*	
35,016	*vs*	0+2×492
35,019	*vs*	
35,049	*ms*	0+953+62
35,052	*ms*	
35,072	*ms*	0+797+282−42
35,075	*ms*	
35,079	*ms*	0+2×492+62,
35,081	*ms*	0+797+292−42
35,092	*ms*	0+567+492
35,094	*ms*	
35,114	*vs*	0+797+282
35,117	*vs*	
35,135	*s*	0+1184−2×42
35,138	*s*	
35,173	*ms*	0+1184−42
35,177	*ms*	
35,193	*m*	0+953+292
35,197	*m*	−2×42
35,201	*s*	0+2×797−423
35,205	*s*	
35,216	*vs*	0+1184
35,219	*vs*	
35,223	*m*	0+953+282−42
35,226	*m*	
35,236	*s*	0+953+292−42
35,239	*s*	
35,267	*ms*	0+953+282
35,270	*ms*	
35,277	*vvs*	0+953+292,
35,281	*vvs*	0+1184+62,
		0+797+492−42
A. The Double Bands		
35,298	*ms*	0+2×492+282
35,301	*ms*	
35,304	*ms*	0+2×492+292
35,306		
35,319	*vvs*	0+797+492
35,322	*vvs*	
35,381	*m*	0+797+492+62
35,384	*m*	
35,397	*ms*	0+1446−2×42
35,401	*ms*	
35,437	*m*	0+1446−42
35,441	*m*	
35,464	*m*	0+2×717
35,467	*m*	
35,478	*vvs*	0+1446
35,480	*vvs*	
35,542	*ms*	0+1446+62
35,545	*ms*	
35,552	*m*	0+1184+338,
35,555	*m*	0+953+567
35,626	*vvs*	0+2×797
35,629	*vvs*	
35,690	*s*	0+2×797+62
35,692	*s*	
35,703	*vs*	0+1713−42
35,705.4	*vs*	
35,727	*s*	0+1446+292−42
35,730	*s*	
35,745	*vvs*	0+1713
35,748	*vvs*	
35,755	*s*	0+2×797+2×62
35,758	*s*	
35,783	*vvs*	0+953+797,
35,786	*vvs*	0+1184+567
35,845	*m*	0+953+797+62,
35,849	*m*	0+1184+567+62
35,937	*vs*	0+2×953
35,939	*vs*	
35,953	*ms*	0+1713+292
35,957	*ms*	−2×42
35,993	*ms*	0+1713+292−42
35,996	*ms*	
36,006.2	*ms*	0+1446+953−423
36,009.3	*ms*	
36,024.6	*ms*	0+953+797
36,027.7	*ms*	+282−42
36,067	*s*	0+953+797+282
36,069	*s*	
36,117.7	*s*	0+2×797+292
36,120.7	*s*	
36,221	*ms*	0+1446+492
36,224	*ms*	+292−42
36,229	*vs*	0+1446+797−42,
36,231	*vs*	0+2×953+292,
		0+1184+953+62,
		0+797+953
		+492−42
A. The Double Bands		
36,260	*ms*	0+1446+492+292
36,263.0	*ms*	
36,273.5	*ms*	0+1446+797
36,276	*ms*	
36,336	*m*	0+1446+797+292
36,340	*m*	
36,697	*ms*	0+1713+953
36,700	*ms*	
36,824	*m*	0+1713+797+282
36,828	*m*	
36,933	*m*	0+1713+1184
36,936	*m*	
37,515	*m*	
37,519	*m*	
B. The Single Bands		
33,461	*wB*	
33,530	*m*	
22,583	*wB*	
33,601	*wBD*	
33,664	*mD*	
33,682	*w*	
33,691	*w*	
33,709	*wD*	
33,733	*w*	
33,749	*wD*	
33,790	*w*	
33,796	*w*	
33,816.0	*wB*	
33,831	*wD*	
33,857	*m*	
33,869	*msB*	
33,882	*mB*	
33,892	*mB*	
33,900	*w*	
33,923	*msB*	
33,932	*m*	
33,999	*w*	
34,023	*sD*	
34,047	*w*	
34,050.7	*ms*	
34,055	*m*	
34,066	*mBD*	
34,087	*mBD*	
34,101	*m*	
34,104	*m*	
34,138.1	*w*	
34,148.8	*m*	
34,153	*w*	
34,158	*m*	
34,168	*mB*	
34,180	*w*	
34,215.4	*w*	
34,227	*m*	
34,248	*msB*	
34,251	*m*	
34,257	*mB*	
34,263	*wB*	
34,266.9	*mB*	
34,276.3	*msD*	
34,289	*m*	
34,292	*ms*	
34,332	*m*	
34,336	*m*	
34,341	*w*	
34,351	*wBD*	
34,362	*mD*	
34,380	*ms*	
34,387	*wD*	
34,394	*vw*	
34,416	*w*	
34,426	*w*	
34,434	*wB*	
34,448	*wD*	
34,458	*msBD*	
34,474.6	*mD*	
34,500	*mD*	
34,550	*mBD*	

TABLE I.—*Continued.*

Frequency (cm^{-1})	Intensity	Assignment
B. The Single Bands		
34,557	*m*	
34,570	*m*	
34,580	*mD*	
34,582	*vw*	
34,593	*ms*	
34,640	*wD*	
34,647	*vwD*	
34,655	*wB*	
34,663.9	*wB*	
34,673	*msD*	
34,676.8	*msB*	
34,682	*msB*	
34,686.8	*msB*	0+1184−531
34,690.7	*m*	
34,695.4	*ms*	
34,698	*m*	
34,719.1	*mB*	
34,745	*m*	
34,757.6	*mD*	
34,765	*mBD*	
34,796	*vsB*	0+1184−423
34,823	*msD*	
34,844	*wB*	
34,847	*w*	
34,852	*w*	
34,857	*m*	
34,873	*ms*	
34,878.6	*mD*	
34,886	*w*	
34,898.7	*m*	
34,902	*w*	
34,918	*vw*	
34,936	*mBD*	
34,948.9	*w*	
35,000	*w*	
35,005	*vw*	
35,008	*vw*	
35,030	*w*	
35,039.6	*wD*	
35,055	*m*	
35,126	*mBD*	
35,155	*m*	
35,166	*ms*	
35,210	*m*	
35,231	*w*	
35,246	*w*	
35,253	*mBD*	
35,314.1	*m*	
35,334.8	*ms*	
35,341	*vsB*	0+953+292+62
35,349	*w*	
35,360	*ms*	
35,369	*w*	
35,410	*w*	
35,415	*m*	
35,425.0	*m*	
35,452	*mD*	
35,458	*m*	
35,471	*w*	
35,483	*m*	
35,509	*m*	
35,515	*vw*	
35,526	*msB*	0+2×717+62
35,563	*w*	
35,575	*wB*	
35,585	*sBD*	0+2×797−42
35,603	*msB*	
35,617	*ms*	
35,652	*vw*	
35,656	*vw*	
35,663	*vwBD*	
35,672	*mBD*	
35,686	*ms*	
35,713	*w*	
35,716	*m*	
35,721	*w*	
35,741	*vsB*	0+953+797−42, 0+1184+567−42
35,769.6	*vsB*	0+1446+292
35,776	*m*	
35,793	*w*	
35,797	*m*	
35,804	*m*	
35,812	*s*	
35,821	*vw*	
35,828	*w*	
35,833	*vsB*	
35,840	*m*	
35,854	*m*	
35,876	*msD*	
35,889.4	*mD*	
35,893	*ms*	
35,896.2	*ms*	
35,905.5	*m*	
35,916.3	*m*	
35,922	*w*	
35,930.2	*mD*	
35,948	*w*	
35,965	*mBD*	
35,972	*ms*	
35,981	*vw*	
35,987	*vw*	
36,038	*mB*	0+1713+292
36,049	*mB*	
36,082	*ms*	
36,089	*s*	
36,092.4	*s*	
36,096	*s*	
36,110	*m*	
36,138	*s*	
36,157	*mBD*	
36,170	*sB*	
36,180	*ms*	
36,187	*ms*	
36,190	*ms*	
36,205	*msB*	
36,237	*s*	
36,245	*msB*	
36,253	*msB*	
36,269	*w*	
36,294	*s*	
36,301	*w*	
36,310	*m*	
36,318	*w*	
36,325	*ms*	
36,353	*ms*	
36,371	*ms*	
36,389	*wB*	
36,402.1	*m*	
36,415	*s*	
36,430.9	*ms*	
36,438	*w*	
36,446	*w*	
36,464	*mB*	
36,477	*mB*	
36,493	*msB*	
36,505	*msB*	
36,515	*msB*	
36,526	*msB*	
36,538	*msB*	
36,556	*msD*	
36,568	*mB*	
36,581	*vsB*	
36,608	*mD*	
36,623	*vw*	
36,627	*m*	
36,635.0	*w*	
36,645	*msD*	
36,658	*mD*	
36,672	*mD*	
36,680	*vw*	
36,684	*vw*	
36,689	*mD*	
36,705.8	*mD*	
36,721.0	*msD*	
36,735	*s*	
36,747	*msD*	
36,766.7	*mBD*	
36,786	*ms*	
36,795.9	*mD*	
36,801	*w*	
36,846	*msBD*	
36,858	*m*	
36,881	*msD*	
36,888.8	*msD*	
36,905.5	*m*	
36,916.3	*w*	
36,927	*mBD*	
36,947	*w*	
36,958.8	*m*	
36,976	*w*	
36,992	*m*	
37,004	*m*	
37,018	*vw*	
37,031	*m*	
37,048	*ms*	
37,056	*vw*	
37,071.9	*ms*	
37,082	*m*	
37,090.2	*ms*	
37,106	*m*	
37,113	*m*	
37,121	*mBd*	
37,128	*mB*	
37,136	*m*	
37,151	*vw*	
37,170.9	*m*	
37,180	*m*	
37,187	*vw*	
37,196	*w*	
37,202	*vw*	
37,209	*msD*	
37,227.2	*m*	
37,244.0	*ms*	
37,261	*vw*	
37,279	*w*	
37,291	*vw*	
37,304.4	*mBD*	
37,321	*vw*	
37,353	*vw*	
37,364	*wBD*	
37,369	*vw*	
37,381	*vw*	
37,389.8	*mBD*	
37,410	*vw*	
37,420.6	*vw*	
37,441.6	*wBD*	
37,459	*vw*	
37,468	*vw*	
37,489	*wBD*	
37,532.0	*msBD*	
37,546	*w*	
37,595.4	*m*	
37,611	*w*	
37,622	*wBD*	
37,632	*w*	
37,649	*vw*	
37,671.8	*vw*	
37,683.6	*vw*	
37,718	*vw*	
37,734	*wD*	
37,784.9	*vw*	
37,798.3	*vw*	
37,832.1	*vw*	
37,837	*vw*	
37,882.3	*vw*	
37,885	*vw*	
37,912.3	*vw*	
37,945	*vw*	
37,952	*w*	
37,998.0	*w*	
38,005	*vw*	
38,023	*w*	
38,043	*vw*	
38,064	*w*	
38,071	*vw*	
38,118	*vw*	
38,126	*w*	
38,158	*w*	
38,209	*vw*	
38,221	*vw*	
38,255	*vw*	
38,281	*w*	
38,338	*vw*	
38,388	*vw*	
38,429	*vw*	
38,560	*w*	
38,682	*vw*	
38,783	*vw*	
38,846	*w*	
38,896	*vw*	
38,944	*w*	
39,046	*vw*	
39,216	*vw*	
39,278	*vw*	
39,341	*vw*	
39,441	*w*	
39,483	*w*	

between the two. Masaki has chosen 34,034 cm^{-1} as the 0−0 band while Titeica has assigned the frequency 34,035 to this transition. A strong diffuse band 9 cm^{-1} to the red (34,023) appeared in aniline as was the case for monochlorobenzene. Similar satellites are associated with a number of the other strong doublets.

The first doublet to the red is 42 cm^{-1} from the 0−0 frequency. This might be interpreted as a 1−1 transition between vibrational frequencies 994 in the ground state and 953 in the excited state. This 994 frequency corresponds to 991 reported by Masaki in his ultraviolet investigation, and to the 993 found in the Raman investigations. Since the investigations herein reported were carried out with relatively low aniline pressures, the spectrum did not extend below 656 cm^{-1} to the red of 0−0, and hence 994 was not found. But with 0−2×42 and 0−3×42 occurring in the spectrum, the non-appearance of

TABLE II. The vibration frequencies of aniline. (The letters in parenthesis indicate possible associated ground and excited frequencies.)

Ground State						
Ultraviolet			Symmetric Raman		Excited State	
Masaki	Titeica	This research	Masaki	Kahovec and Reitz	This research	Titeica
—	233	231	—	234	62	147
—	—	—	—	386(*a*)	282	224
421	423	423	—	—	292	291
529	521	531	530	534(*b*)	338(*a*)	
—	—	—	—	615(*c*)	492(*b*)	491
821	821		815	817(*d*)	567(*c*)	505
991			993	994(*e*)	717	
1032			1028	1030	797(*d*)	
				1265(*f*)	953(*e*)	952
				1601(*g*)	1184(*f*)	
					1446(*g*)	
					1713	
						2583

0−994 in considerable strength weakens the above analysis.

The frequencies 231 and 531 were observed by other investigators in the ultraviolet and also in the Raman effect. The frequency 423, while also listed by both Masaki and Titeica, does not appear in Raman data.

The first doublet towards the violet is 62 cm^{-1} from 0−0. This is interpreted as being a $1-1'$[8] transition between 231 in the ground state and 292 in the excited state. The frequencies 338, 492, 567, 797, 953, 1184, and 1446 of the excited state may be tentatively associated with the symmetric Raman lines 386, 534, 615, 817, 994, 1275, and 1601, respectively. The association in the case of the last two frequencies is less certain than the others since this involves rather large drops in frequency of 91 and 155 cm^{-1} in going from the ground to the excited state.

There remains then the frequencies 282, 292, 717, and 1713 unexplained, 292 being also reported by Titeica. The two lower frequencies might be difference frequencies between unassigned levels, however, these are two of the strongest bands in the spectrum. Similarly 717 and 1713 might be possible combination frequencies.

This leaves 1030 as the only symmetric Raman frequency that has not been associated with any frequency in the excited state. Since Masaki also found this as a 1−0 transition in the ultraviolet spectrum, its existence cannot be doubted. A possible association is the 984 frequency, which has here been identified as 2×492.

Several of the stronger bands which appeared single have been given as assignment based on frequencies used in the analysis of the doublet spectrum.

Acknowledgment is hereby made for the special Graduate Research Fund grant given for construction of the spectrograph, and for supplementary grants made by the Research Institute of The University of Texas in support of this work.

[8] The $1-1'$ transition is to be interpreted as a transition between one mode of vibration in the ground state to a different mode of vibration in the excited state.

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The Thermodynamics of High-Polymer Solutions: I. The Free Energy of Mixing of Solvents and Polymers of Heterogeneous Distribution*

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The theories of Flory and Huggins for the free energy of mixing of a homogeneous chain polymer of uniform molecular weight with a single uniform solvent have been extended to the case of a polymer mixture of varying chain lengths with a mixture of solvents. By making the similar assumptions as those of Huggins, and utilizing familiar statistical mechanical methods, the partial molal free energy of mixing of the solvent is found to be

$$\overline{\Delta F}_0 = RT[\ln \phi_0 + (1-\phi_0)(1-1/\bar{m}_N) + \mu(1-\phi_0)^2],$$

where ϕ_0 is the volume fraction of solvent, $\bar{m}_N$ a simple function of the number average molecular weight, and μ a constant characteristic of the polymer-solvent mixture (consisting largely of a heat term, but also including γ, the coordination number of the rubber segments). By assuming that a mixture of two solvents behaves like a new homogeneous liquid a method of calculating μ for such mixtures is developed. Applications of these formulas to solubility and fractionation are shown in a subsequent article.

INTRODUCTION

THE free energy relations of high-polymer solutions were first calculated independently by Flory[1] and Huggins[2] for the case of a homogeneous chain polymer of uniform molecular weight in a single uniform solvent. In practice, however, one is never dealing with a polymer sample in which all the molecules have the same molecular weight, but rather with a mixture of molecular weights, forming a virtually continuous distribution. If, on the other hand, one intends to extend the thermodynamic treatment of such solutions to the problems of fractionation and precipitation it is of interest to extend the treatment to a solvent medium consisting of a mixture of two pure solvents. The purpose of this and the following paper is to extend the theory to these two cases and to give a thermodynamic treatment of solubility, fractionation, and precipitation. Although the final results of Flory and Huggins are fairly analogous, we preferred to base our derivations upon the development of Huggins who, in our opinion, makes less, and more justifiable, assumptions concerning the nature of the rubber molecule than does Flory.

1. Entropy of Mixing of Chains of Varying Length with a Solvent

Suppose a mixture consisting of n_1 molecules of molecular weight m_1 (in units of arbitrary submolecules, the density of all molecular weight fractions being taken as the same),[3] n_2 molecules of molecular weight m_2, n_3 of m_3, etc. Then the total number of sites, for submolecules and solvent molecules is

$$N = N_0 + n_1 m_1 + n_2 m_2 + \cdots + n_f m_f, \qquad (1)$$

where N_0 = the number of sites occupied by the solvent molecules.

In order to calculate the entropy of this system we have to determine the total number of configurations. We shall proceed in the same way as Huggins did for the binary system.[4]

Suppose now that n_1 molecules of the type m_1, n_2 of the type m_2, etc., up to n_{i-1} of the type m_{i-1} have already been put into the "lattice" as well as $K-1$ molecules of the type m_i.

Let $\nu_{i,K,l}$ be the number of alternative sites available for the lth segment of the Kth molecule of the type m_i. Then for the first segment of the Kth molecule of the m_i type

$$\nu_{i,K,1} = N(1-f_j), \qquad (2)$$

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[1] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

[2] M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).

[3] Each submolecule is considered as the same size as a molecule of solvent so that m_i is in reality the ratio of the molecular volume of the polymer molecule of molecular weight M_i and the molecular volume of the solvent V_0 or $m_i = M_i/\rho V_0$. If ρ, the density of the polymer, is considered as independent of the chain length, then m_i is, for any given solvent, directly proportional to and therefore a measure of the molecular weight.

[4] There is, however, one difference between our treatment and that of Huggins. Huggins considers each molecule of molecular volume m as consisting of l freely orienting segments each of them composed of p submolecules. Since, however, in the final formulation l and p appear only as the product $lp = m$, we did not use this decomposition and consider simply the molecule as composed of m segments.

where f_j=the fraction of the total number of sites already occupied.

$$f_j=\frac{\sum_{i=1}^{i-1} n_i m_i+(K-1)m_i}{N}. \tag{3}$$

Once the first submolecule is placed in a site S_0, the position of the other submolecule is greatly limited. Huggins points out that if the immediately adjacent site S_1 is occupied, two of the sites immediately adjacent to S_1 must also be occupied, provided S_1 is not the end of the chain.[5] Hence the probability that both S_1 and S_0 are occupied by adjacent molecules of a previous chain is:

$$P=2f_j/\gamma, \tag{4}$$

where γ is the "coordination number," i.e., the number of neighbor sites around each site. But in our case S_0 cannot have been occupied by a submolecule of a previous chain since we assumed that it is occupied by a first submolecule of the present chain. Hence the probability that S_1 is unoccupied and free for the second submolecule is greater than (4) and is

$$P=[1-f_j]/[1-(2f_j/\gamma)], \tag{5}$$

and the number of sites available for the second submolecule is

$$\nu_{j,K,2}=\gamma(1-f_j)/[1-(2f_j/\gamma)], \tag{6}$$

and similarly for the third submolecule

$$\nu_{j,K,3}=(\gamma-1)(1-f_j)/[1-(2f_j/\gamma)], \tag{7}$$

and so on.

Hence for the Kth chain of the ith type the total number of distinguishable configurations is

$$\nu_{i,K}=(N/\sigma)(1-f_j)\gamma(\gamma-1)^{m_i-2}[1-f_j]/[1-(2f_j/\gamma)]^{m_i-1}, \tag{8}$$

where σ is the symmetry number of the chain (i.e., 2 if the ends are interchangeable), or introducing the definition of f_j (3)

$$\nu_{i,K}=\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma}\,\frac{(N-\sum_{i=1}^{i-1} n_i m_i-(K-1)m_i)^{m_i}}{(N-2/\gamma[\sum_{i=1}^{i-1} n_i m_i-(K-1)m_i])^{m_i-1}}.$$

Then, the total number of configurations for the n_i molecules of the ith type may be written as:

$$\prod_{k=1}^{n_i}\nu_{i,k}=x\left[\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma}\right]^{n_i}\frac{\prod_{k=0}^{n_i-1}(N-\sum_{i=1}^{i-1} n_i m_i-km_i)^{m_i}}{\prod_{k=0}^{n_i-1}(N-2/\gamma[\sum_{i=1}^{i-1} n_i m_i+km_i])^{m_i-1}}. \tag{9}$$

Taking the logarithm and replacing the summations by integrals (equivalent to the approximation of Sterling's formula),

$$\ln\prod_{K=1}^{n_i}\nu_{i,K}=n_i\ln\left(\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma}\right)+m_i\int_0^{n_i}\ln(N-\sum_{i=1}^{i-1} n_i m_i-Km_i)dK$$

$$-(m_i-1)\int_0^{n_i}\ln(N-2/\gamma[\sum_{i=1}^{i-1} n_i m_i-Km_i])dK. \tag{10}$$

[5] For long molecules, as Huggins has shown, this possibility introduces only a negligible correction.

Integrating

$$\ln \prod_{K=1}^{n_i} \nu_{i,K} = n_i \ln \left(\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right) - n_i m_i - (N - \sum_{i=1}^{i} n_i m_i) \ln (N - \sum_{i=1}^{i} n_i m_i)$$

$$+ (N - \sum_{i=1}^{i-1} n_i m_i) \ln (N - \sum_{i=1}^{i-1} n_i m_i) + \frac{(m_i - 1)}{2m_i} \gamma [(N - 2/\gamma \sum_{i=1}^{i} n_i m_i) \ln (N - 2/\gamma \sum_{i=1}^{i} n_i m_i)$$

$$- (N - 2/\gamma \sum_{i=1}^{i-1} n_i m_i) \ln (N - 2/\gamma \sum_{i=0}^{i-1} n_i m_i) + 2/\gamma n_i m_i]. \quad (11)$$

The total number of distinguishable configurations for the whole system is

$$W = [(\prod_{i=1}^{i} \prod_{K=1}^{n_i} \nu_{i,K})(\prod \nu_0)]/[(\prod_i n_i!)(n_0!)] = [\prod_i \prod_{K=1}^{n_i} \nu_{i,K}]/[\prod_i n_i!], \quad (12)$$

and the entropy of the system

$$S/k = \ln W = \sum_i \ln \prod_{K=1}^{n_i} \nu_{i,K} - \sum_i n_i \ln n_i + \sum n_i. \quad (13)$$

Substituting (11) in (13) and simplifying

$$S/k = \sum_i n_i \ln \left[\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right] - \sum_i n_i \ln n_i/N - N_0 \ln N_0/N + \gamma/2 (N - 2/\gamma \sum_i n_i m_i)$$

$$\times \ln \left(1 - 2/\gamma \frac{\sum_i n_i m_i}{N} \right) - \gamma/2 \sum_i [N/m_i][(1 - 2/\gamma N \cdot \sum_{i=1}^{i} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i} n_i m_i)$$

$$- (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i)]. \quad (14)^6$$

So far no new assumption or approximation has been made beyond the ones used in Huggins" theory. However, in order to go further than Eq. (14) one has to make the following simplification: the last term of the Eq. (14) is very small since it involves essentially a difference of sums extended once to the ith molecule type, once to the $(i-1)$th type. If we now assume that any given molecular weight fraction is small, $n_i m_i \ll \sum n_i m_i$ it is legitimate to expand the logarithms in series and cancel all but the first term. Then this term becomes

$$-\gamma/2 \cdot \sum_i N/m_i [(1 - 2/\gamma N \cdot \sum_{i=1}^{i} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i} n_i m_i)$$

$$- (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i) \ln (1 - 2/\gamma N \cdot \sum_{i=1}^{i-1} n_i m_i)] \leqq + \sum_i n_i. \quad (15)$$

Equation (14) has taken then the simplified form:

$$S/k \leqq \sum_i n_i \ln \left[\frac{\gamma(\gamma-1)^{m_i-2}}{\sigma} \right] - \sum_i n_i \ln n_i/N - N_0 \ln N_0/N$$

$$+ \gamma/2 (N - 2/\gamma \sum_i n_i m_i) \ln (N - 2/\gamma \sum_i n_i m_i) + \sum_i n_i. \quad (16)$$

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[6] If one now assumes that only molecules of one chain length are present, $n_1 = N_r$, $n_2 = n_3 = \cdots = 0$ then Eq. (14) reduces to:

$$S/k = N_r \ln \left[\frac{\gamma(\gamma-1)^{m-2}}{\sigma} \right] - N_r \ln \frac{N_r}{N_0 + mN_r} - N_0 \ln \frac{N_0}{N_0 + mN_r} + (m-1)[\gamma/2m \cdot N_0 + (\gamma/2 - 1) N_r] \ln \left[\frac{N_0 + (1 - 2/\gamma) mN_r}{N_0 + mN_r} \right],$$

which is identical with the equation derived by Huggins.

The entropy of mixing is of course

$$\Delta S_{\text{mix}} = S - S_0 - \sum S_i, \tag{17}$$

where S_0 and S_i are the entropies of pure solvent and pure rubber fraction respectively. Substituting in Eq. (16) the conditions $n_1 \neq 0$ and $n_2 = n_3 = n_4 = \cdots = 0$; $n_2 \neq 0$ and $n_1 = n_3 = n_4 = \cdots = 0$, etc., and $N_0 = 0$ separately one finds

$$S_0 = 0, \tag{18}$$

$$S_i/k = n_i \ln [\gamma(\gamma-1)^{m_i-2}]/\sigma + n_i \ln m_i + (\gamma/2-1) n_i m_i \ln (1-2/\gamma) + n_i. \tag{19}$$[7]

After subtraction one obtains the entropy of mixing.

$$\Delta S_{\text{mix}}/k = -\sum_i n_i \ln n_i m_i/N - N_0 \ln N_0/N + \gamma/2(N - 2/\gamma \sum_i n_i m_i) \ln (N - 2/\gamma \sum_i n_i m_i) - (\gamma/2-1) \ln (1-2/\gamma) \cdot \sum_i n_i m_i. \tag{20}$$

After partial differentiation and some simplifications, Eq. (20) yields the partial molal entropies.

$$\frac{\overline{\Delta S_0}}{R} = \frac{\partial(\Delta S_{\text{mix}}/R)}{\partial N_0} = +\sum_i \frac{n_i}{N} - \ln \frac{N_0}{N} - \frac{N_0}{N} + \frac{\gamma}{2}\left[\ln\left(1 - \frac{2}{\gamma N}\sum_i n_i m_i\right) + \frac{2}{\gamma N}\sum_i n_i m_i\right], \tag{21a}$$

$$\frac{\overline{\Delta S_i}}{R} = \frac{\partial(\Delta S_{\text{mix}}/R)}{\partial n_i} = +m_i \sum_i \frac{n_i}{N} - \ln \frac{n_i m_i}{N} - 1 + \frac{m_i N_0}{N} + \left(\frac{\gamma}{2} - 1\right) \ln \left(\frac{1 - \frac{2}{\gamma N}\sum_i n_i m_i}{1 - \frac{2}{\gamma}} \right) - m_i \left(1 - \frac{\sum_i n_i m_i}{N}\right). \tag{21b}$$

If we introduce now measurable values, e.g., volume fractions, one has the relation

$$N_0/N = \phi_0, \quad n_i m_i/N = \phi_i, \quad \sum_i n_i m_i/N = \sum_i \phi_i = 1 - \phi_0.$$

Further, the number average molecular weight (in units of submolecules) is:

$$\bar{m}_N = \sum_i n_i m_i / \sum_i n_i = (\sum_i \phi_i)/[\sum_i (\phi_i/m_i)] \tag{22}$$

and hence

$$\sum_i n_i/N = 1 - \phi_0/\bar{m}_N. \tag{23}$$

Introducing this definition in Eq. (21), expanding the logarithms in the last term and neglecting the terms in ϕ^3 or higher, one obtains finally:

$$\overline{\Delta S_0} = -R[\ln \phi_0 + (1 - 1/\bar{m}_N)(1-\phi_0) + 1/\gamma(1-\phi_0)^2]; \tag{24}$$

$$\overline{\Delta S_i} = -R[\ln \phi_i + 1 - m_i\phi_0 - (m_i/\bar{m}_N)(1-\phi_0) + (m_i/\gamma)\phi_0^2]. \tag{25}$$

Several remarks can be made concerning Eqs. (24) and (25). (1) It is not apparent why the last term in Eq. (25) is $m_i/\gamma \cdot \phi_0^2$ and not $m_i\phi_0^2/(\gamma-2)$ as would follow from the calculation given above. This substitution is made by analogy to Huggins, who gives no justification for it. Actually, the denominator has to be γ and not $\gamma - 2$ if Eqs. (24) and (25) are to be consistent and satisfy the Gibbs

[7] This is what Flory calls the disorientation entropy of the polymer mixture.

relation. Presumably this substitution corrects for the fact that the expansions in Eqs. (21a) and (21b) are not exactly equivalent, the terms in (21a) being all positive while the terms in (21b) are alternately positive and negative. Hence when the higher terms are neglected, the same degree of approximation is not reached. (2) For a binary system $m_i = \bar{m}_n = m$ and this reduces to the familiar equations of Huggins:

$$\overline{\Delta S_0} = -R[\ln \phi_0 + (1-1/m)\phi_r + (1/\gamma)\phi_r^2]; \quad (26a)$$

$$\overline{\Delta S_r} = -R[\ln \phi_r - (m-1)\phi_0 + (m/\gamma)\phi_0^2]. \quad (26b)$$

(3) The partial molal entropy of the solvent does not depend on the molecular weight distribution of the high polymer but only on the number average molecular weight $\bar{m}_N$, while the partial molal entropy of the polymer depends on both $\bar{m}_N$ and the molecular weight distribution. This is important because it shows that the colligative properties (osmotic pressure, vapor pressure lowering, freezing point lowering) are independent of the actual molecular weight distribution of the polymer and always permit determination of the number average molecular weight.

2. Heat of Mixing

No exact formula exists for the time being for the computation of the partial molal heats of mixing. However, at least in the case of non-polar polymers, it was shown by the experiments of Gee and Treloar[8] and by some unpublished experiments of the authors that the total heat of mixing can be fairly well represented by a Scatchard-Hildebrand formula, i.e.,

$$\Delta H_{\text{mix}} = V_m(\alpha_0 - \alpha_r)^2 \phi_0 \phi_r, \quad (27a)$$

where α_0 and α_r are the square roots of the cohesive energies (internal heats of vaporization) per unit volume:[9]

$$\begin{aligned} \alpha_0 &= (E_{0(\text{coh})}/V_0)^{\frac{1}{2}} = (\lambda_0 - RT/V_0)^{\frac{1}{2}}, \\ \alpha_r &= (E_{r(\text{coh})}/V_r)^{\frac{1}{2}} = (\lambda_r - RT/V_r)^{\frac{1}{2}}, \end{aligned} \quad (28)$$

and V_m the molecular volume of the mixture

$$V_m = X_0 V_0 + X_r V_r = V_0 V_r/(\phi_0 V_r + \phi_r V_0). \quad (29)$$

[8] G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

[9] The subscript 0 represents the solvent, and r the rubber (polymer).

In order to expand the Scatchard-Hildebrand formula to mixtures of polymers and solvents, let us recall at this point the basic assumptions from which the formula (27) is derived. The cohesive energy of a mixture is supposed to be the sum of three types of interaction, writing each in terms of the volume fraction

$$(E_{\text{coh}})_{\text{mix}} = (A_{11}\phi_1^2 + 2A_{12}\phi_1\phi_2 + A_{22}\phi_2^2) V_m, \quad (30)$$

where A_{11}, A_{12} and A_{22} are constants characteristic of the interaction between the molecules, A_{11} and A_{22} between molecules of the same type, A_{12} between molecules of different types.

For the pure components,

$$\begin{aligned} (E_{\text{coh}})_1 &= A_{11}V_1; \quad (E_{\text{coh}})_2 = A_{22}V_2; \\ &= \alpha_1^2 V_1; \qquad\quad = \alpha_2^2 V_2. \end{aligned} \quad (31)$$

For the interaction of two different type molecules, it is now assumed

$$A_{12} = (A_{11}A_{22})^{\frac{1}{2}}. \quad (32)$$

This assumption was first made by van der Waals. The quantum mechanical treatment[10] of the intermolecular forces of non-electrostatical nature corrected this formula to

$$A_{12} \leqq (A_{11}A_{22})^{\frac{1}{2}}. \quad (33)$$

Assuming Eq. (32) to be valid, Eq. (30) can hence be written

$$(E_{\text{coh}})_{\text{mix}} = [(A_{11})^{\frac{1}{2}}\phi_1 + (A_{22})^{\frac{1}{2}}\phi_2)]^2, \quad (34)$$

which, after subsequent transformation, under the additional assumption that the mixture is ideal in the sense that volumes of the components are additive, leads to Eq. (27).

In the case when one of the components is polar the relation of Eq. (32) can no longer be expected to hold even approximately. Nevertheless, experiments have shown that, in this case, the total heat of mixing can be roughly represented by

$$\Delta H_{\text{mix}} = K V_m(\alpha_0 - \alpha_r)^2 \phi_0 \phi_r, \quad (27b)$$

where K is a constant somewhat larger than unity and correcting for the fact that always in this case $A_{12} < (A_{11}A_{22})^{\frac{1}{2}}$. For mixtures of non-polar compounds $K = 1$.

It must be emphasized that the cohesive energy is essentially a localized affair determined by the

[10] F. London, Zeits. f. physik. Chemie **B11**, 222 (1930).

interactions between adjacent atoms and groups of atoms belonging to the several components. It is essentially the interaction between the submolecules of the polymer and the molecules of the solvent, and is independent of the actual chain length.

Let us apply now Eq. (27a) or (27b) to the complex system of a mixture of a solvent and of polymer molecules of differing chain length. From the outset we can assume that α_r is the same for all the different rubber molecules and that therefore there is no heat of mixing from this source. The only heat of mixing developed is that between the solvent and the polymer which we may treat for our purposes as one component.

Introducing the molar fractions, Eq. (27a) becomes

$$H_{\text{mix}}=(X_0V_0+\sum_i X_im_iV_0)(\alpha_0-\alpha_r)^2 \times\frac{X_0V_0(\sum_i X_im_iV_0)}{(X_0V_0+\sum_i X_im_iV_0)^2}$$
$$=V_0(\alpha_0-\alpha_r)^2\frac{X_0\sum X_im_i}{(X_0+\sum X_im_i)}. \quad (35)$$

The partial molar heats of mixing are obtained by differentiation of Eq. (35).

$$\overline{\Delta H}_0=\left(\frac{\partial H_{\text{mix}}}{\partial X_0}\right)$$
$$=V_0(\alpha_0-\alpha_r)^2\frac{(\sum X_im_i)^2}{(X_0+\sum X_im_i)^2}$$
$$=V_0(\alpha_0-\alpha_r)^2(1-\phi_0)^2; \quad (36)$$

$$\overline{\Delta H}_i=\left(\frac{\partial H_{\text{mix}}}{\partial X_i}\right)$$
$$=V_0(\alpha_0-\alpha_r)\frac{m_i(X_0)^2}{(X_0+\sum X_im_i)^2}$$
$$=m_iV_0(\alpha_0-\alpha_r)^2\phi_0^2. \quad (37)$$

In order to be able to treat the solubility and other properties of a polymer in a mixture of two solvents, we have to extend the formula for the heat of mixing in order to include this case. We found that solvent mixtures can be treated with a fair degree of accuracy assuming the mixture of the two solvents to behave as a homogeneous liquid,[11] with respect to the polymer, this new "liquid" having characteristic values of α and V, α_m and V_m. The values of α_m and V_m can be obtained from the theory of heat of mixing developed above (Eq. 34).

$$(E_{\text{coh}})_m/V_m=\alpha_m^2=((A_{11})^{\frac{1}{2}}\phi_1+(A_{22})^{\frac{1}{2}}\phi_2), \quad (38)$$

or

$$\alpha_m=\phi_1\alpha_1+\phi_2\alpha_2=\alpha_1+\phi_2(\alpha_2-\alpha_1), \quad (39)$$

while

$$V_m=V_1V_2/\phi_1V_2+\phi_2V_1 =V_1[(1+\phi_2V_2/(V_1-V_2))]. \quad (40)$$

3. Partial Molal Free Energy

We are now able to express the partial molal free energies of the system considered: a mixture of polymer molecules of different molecular weight and of one or two solvents.

Combining Eqs. (24) and (25) with (36) and (37) respectively, we obtain

$$\overline{\Delta F}_0=RT[\ln\phi_0+(1-\phi_0)(1-1/\bar{m}_N) +\mu(1-\phi_0)^2], \quad (41)$$

$$\Delta F_i=RT[\ln\phi_i+1-m_i\phi_0 -(m_i/\bar{m}_N)(1-\phi_0)+m_i\mu\phi_0^2], \quad (42)$$

where $\mu=1/\gamma+KV_0(\alpha_0-\alpha_r)^2/RT$ in the case of a simple solvent and

$$\mu_m=1/\gamma+\frac{KV_1(\alpha_1-\alpha_r)^2}{RT} \times\left[1+\phi_2\left(\frac{\alpha_2-\alpha_1}{\alpha_1-\alpha_r}\right)\right]^2\Big/\left[1+\phi_2\frac{V_1-V_2}{V_2}\right], \quad (43)$$

in the case of a mixture of solvents (1) and (2).

In the following paper these expressions will be applied to the problems of solubility and fractionation of a rubber-like polymer.

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[11] This can be true only if the interaction of the solvents with the polymer is of second order in comparison with the interaction between the two solvents.

The Thermodynamics of High-Polymer Solutions: II. The Solubility and Fractionation of a Polymer of Heterogeneous Distribution*

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The free energy relations for heterogeneous molecular weight distributions developed in Part I, are applied to problems of solubility and fractionation. Critical conditions for solubility are obtained. A rigorous expression for the solubility is derived, although certain approximations are made to facilitate calculation, and to permit extension to polymers which are part "gel." Following the same methods the thermodynamic equilibria involved in fractionation are described by mathematical expressions which permit a comparison of the extraction and precipitation methods. The effectiveness of fractionation is shown to be strongly dependent upon concentration.

INTRODUCTION

FLORY[1] and Huggins[2] first developed theories of the entropy of mixing of polymers of uniform molecular weight with solvents and soon thereafter[3,4] extended their treatment to include the solubility of such homogeneous polymers. Later, using a modified form of the Flory theory, Gee[5] attempted to give a rough treatment of fractionation. Until now, however, no systematic treatment has been given for polymers consisting of a heterogeneous distribution of chain lengths. Such distributions are to be found in both natural and synthetic rubbers and in all similar chain polymers.

It has been shown in Part I[6] that in a mixture of solvent with such a heterogeneous polymer, the partial molal free energies of mixing of the solvent $\overline{\Delta F_0}$ and of the ith fraction of the polymer $\overline{\Delta F_i}$ may be represented as:

$$\overline{\Delta F_0}=RT\left[\ln\phi_0+(1-\phi_0)\left(1-\frac{1}{\bar{m}_N}\right)+\mu(1-\phi_0)^2\right], \quad (1)$$

$$\overline{\Delta F_i}=RT\left[\ln\phi_i+1-\frac{m_i}{\bar{m}_N}(1-\phi_0)-m_i\phi_0+\mu m_i\phi_0^2\right], \quad (2)$$

where ϕ_0 and ϕ_i are the volume fractions of solvent and ith fraction respectively.

m_i is the ratio of the molecular volumes of the ith fraction V_i and that of the solvent V_0 and, assuming that the density of the polymers is independent of the chain length, a direct measure of the molecular weight.

$$m_i=V_i/V_0=M_i/\rho_r V_0. \quad (3)$$

$\bar{m}_N$ is the number average m, defined as

$$\bar{m}_N=\frac{\sum_i n_i m_i}{\sum_i n_i}=\frac{\sum_i m_i}{\sum_i m_i/\phi_i}, \quad (4)$$

and related to the number average molecular weight by a relation similar to Eq. (3).

μ is a constant for any given system, consisting of the heat of mixing and a term from the entropy, such that

$$\mu=1/\gamma+KV_0(\alpha_0-\alpha_r)^2/RT, \quad (5)$$

where γ = the coordination number of the segments (about 3–4), α_0, α_r = constants for the rubber (polymer) and the solvent (the square root of the internal energy of vaporization per cc) and K an empirical constant relating to the polarity of the substances in the mixture.[7]

* The major portion of the following work was done on a grant from the Rubber Reserve Company for fundamental research in the field of synthetic rubber.

[1] P. J. Flory, J. Chem. Phys. 9, 660 (1941).
[2] M. L. Huggins, J. Chem. Phys. 9, 440 (1941).
[3] P. J. Flory, J. Chem. Phys. 10, 51 (1942).
[4] M. L. Huggins, J. Phys. Chem. 46, 151 (1942); Ann. N. Y. Acad. Sci. 43, 1 (1942).
[5] G. Gee, Trans. Faraday Soc. 38, 276 (1942).
[6] R. L. Scott and M. Magat, J. Chem. Phys. 13, 172 (1945).
[7] For a more comprehensive discussion of these constants, see Part I.

Equation (1) is identical with that for the free energy of the solvent in a binary system as derived by Huggins, with the exception that $\bar{m}_N$ replaces m. Equation (2), however, is not identical with that of the rubber in the homogeneous system.

A. Solubility of a Polymer of Distribution $f(m)$: Distribution of a Fraction of Molecular Weight m_i Between Solution and Swollen Precipitate

From Eqs. (1) and (2), one may deduce the solubility conditions and the distribution of the rubber between two phases.

If one plots $\overline{\Delta F_0}$ against decreasing ϕ_0, one finds that for sufficiently small values of μ, $\overline{\Delta F_0}$ decreases uniformly, signifying complete miscibility of solvent and polymer. (Fig. 1.)[8] With a larger value of μ (that is, a larger heat of mixing), however, the curve shows a minimum and a maximum indicating only partial miscibility. There will therefore be a critical value of μ, μ_c, at which the solution breaks into two phases. For this value the curve will show a point of inflection, and applying the familiar conditions that, here, the first and second derivatives of $\overline{\Delta F_0}$ with respect to ϕ_0 must vanish, one finds:

$$\mu_c=(1/\gamma)+(KV_0(\Delta\alpha)^2/RT)$$
$$=1/2[1+(1/\bar{m}_N)^{\frac{1}{2}}]^2. \quad (6)$$

This is identical with the similar equation,[3,4] for a homogeneous polymer except that $\bar{m}_N$ replaces m. In short, all the critical conditions are the same as those for a binary system if one utilizes the number average molecular weight. These critical conditions depend only on $\bar{m}_N$ and not on the precise nature of the distribution function, which may correspond either to a fairly narrow, homogeneous fraction, or to a very broad distribution.

The critical point corresponds also to a critical value of ϕ_0 and of ϕ_r (the volume fraction of the total rubber.)

$$(\phi_0)_c=\frac{\bar{m}_N}{1+\sqrt{\bar{m}_N}}=\frac{1}{1+(1/\sqrt{\bar{m}_N})}; \quad (7a)$$

$$(\phi_r)_c=(\sum_i \phi_i)_c=\frac{1}{1+\sqrt{\bar{m}_N}}. \quad (7b)$$

Similarly one may speak of a critical solution temperature T_c or a critical value of $(\alpha_0-\alpha_r)$, $(\Delta\alpha)_c$.

$$T_c=\{KV_0(\Delta\alpha)^2\}/\{R[1/2(1+(1/\sqrt{\bar{m}_N}))^2 -(1/\gamma)]\}; \quad (8)$$

$$(\Delta\alpha)_c=\{RT[1/2(1+(1/\sqrt{\bar{m}_N}))^2 -(1/\gamma)]\}/KV_0. \quad (9)$$

Certain consequences follow immediately from these equations: (1) As pointed out above, the critical point is dependent only upon the number average molecular weight. Since, for values of μ less than μ_c, no separation of a rubber phase is possible, it is clear that the presence of low molecular weight material in the polymer tends to keep the high molecular weight material in solution by decreasing the value of $\bar{m}_N$. In short, *low molecular weight material actually makes the higher fractions more soluble.* This factor is crucial

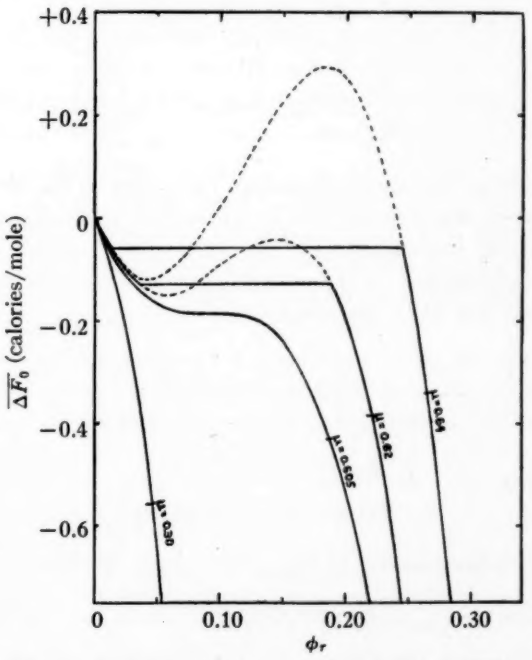

FIG. 1. Partial molal free energy of solvent $\overline{\Delta F_0}$ as a function of μ and ϕ_r, the volume fraction of rubber. $\bar{m}_N=100$ ($\bar{m}_N \leqq 10{,}000$).

[8] For identical curves for polymers of homogeneous distribution, see M. L. Huggins, *Cellulose and Cellulose Derivatives*, edited by Ott (Interscience Publishers, Inc., New York), p. 893.

in any consideration of fractionation or precipitation curves. (2) Since μ_c is inversely proportional to T (Eq. (5)), the solubility increases with an increase in temperature. (3) If for a given rubber-solvent system, $(\alpha_0-\alpha_r)$ is less than the critical $(\Delta\alpha)_c$ in Eq. (9), the rubber and solvent are necessarily completely miscible in all proportions.

To determine the solubility at any other point than at the critical point, one must utilize the equilibrium conditions between the two phases:

$$\overline{\Delta F_0}=\overline{\Delta F_0}', \tag{10}$$

$$\overline{\Delta F_i}=\overline{\Delta F_i}', \tag{11}$$

where the prime represents the swollen rubber phase.

There are, of course, i simultaneous equations of the type of Eq. (11), one for each distinct fraction.

In other words

$$\ln\phi_0+1-\phi_0-\frac{1-\phi_0}{\bar{m}_N}+\mu(1-\phi_0)^2 = \ln\phi_0'+1-\phi_0'-\frac{1-\phi_0'}{\bar{m}_N'}+\mu(1-\phi_0')^2; \tag{12}$$

$$\ln\phi_i+1-\frac{m_i}{\bar{m}_N}(1-\phi_0)-m_i\phi_0+m_i\mu\phi_0^2 = \ln\phi_i'+1-\frac{m_i}{\bar{m}_N'}(1-\phi_0')-m_i\phi_0'+m_i\mu\phi_0'^2. \tag{13}$$

Note that the distribution functions in the two phases are presumed to be different; hence $\bar{m}_N'$ is not the same as $\bar{m}_N$.

Solving Eq. (13) for $\ln\phi_i'/\phi_i$ and substituting from Eq. (12), one obtains

$$\ln\frac{\phi_i'}{\phi_i}=m_i\left[2\mu(\phi_0-\phi_0')-\ln\frac{\phi_0}{\phi_0'}\right], \tag{14}$$

or

$$\phi_i'/\phi_i=\exp(Am_i), \tag{15}$$

where

$$A=2\mu(\phi_0-\phi_0')-(\ln\phi_0/\phi_0').$$

A relation similar to Eq. (14) is given by Schulz:[9]

$$C=Ke^{-P(A+B\gamma)/R\theta}, \tag{16}$$

where C = solubility of material of molecular weight M; P = degree of polymerization of polymer $= M/M_0$; M_0 = molecular weight of monomer; γ = concentration of precipitant (not the γ of Part I of this paper[6]); θ = a temperature function; A, B, K = constants.

This equation yields the same exponential dependence of the solubility on the molecular weight as in Eq. (15), but in our opinion, the assumptions made in the derivation are faulty, and the significance of the constants uncertain. Schulz's work is important, however, as the first attempt to treat the problem of solubility and fractionation from a thermodynamic standpoint.

Equation (15) represents the fundamental basis of the theory of solubility and fractionation presented in the following pages. For any given system, A is a constant; and, therefore, Eq. (15) may be used as a strictly valid relation, showing the distribution of material of different molecular weights between the solution and the rubber phases.

We may now undertake to express the solubility. Let the actual distribution of molecular weights be represented by a distribution function:

$$dw_i=f(m)dm_i, \tag{17}$$

where dw_i is the fraction[10] of the total rubber of molecular weight m_i and $f(m)$ is a normalized function, such that

$$\int_0^\infty f(m)dm=1. \tag{18}$$

What is the solubility if a certain volume v_r of this rubber is placed in a volume v_0 of a certain solvent? The total amount of rubber, v_i in any given fraction is the sum of the amounts in the solution phase and in the swollen rubber phase.

$$v_i=\phi_i v_s+\phi_i' v_p, \tag{19}$$

where $v_i=v_r dw_i=v_r f(m)dm_i$; v_s = volume of solution phase; v_p = volume of swollen rubber phase. Substituting the condition of Eq. (15),

$$v_i=\phi_i v_s+\phi_i v_p\exp(Am_i); \tag{20}$$

$$\phi_i=v_i/(v_s+v_p e^{Am_i})=v_r f(m)dm_i/(v_s+v_p\exp(Am_i)). \tag{21}$$

[9] G. V. Schulz, Zeits. f. physik. Chemie **A179**, 321 (1937).

[10] Either weight fraction or volume fraction, since the density of the rubber is presumed to be uniform, independent of molecular weight. This assumption however, is only approximate. It means in reality that we neglect the end atoms when compared to the length of the chain. For high molecular weights, this is obviously justified.

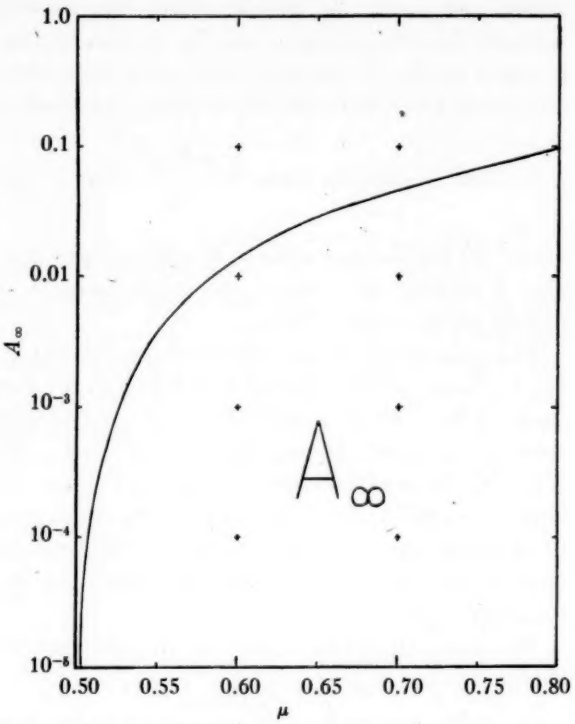

FIG. 2. The approximation constant A_∞ as a function of μ.

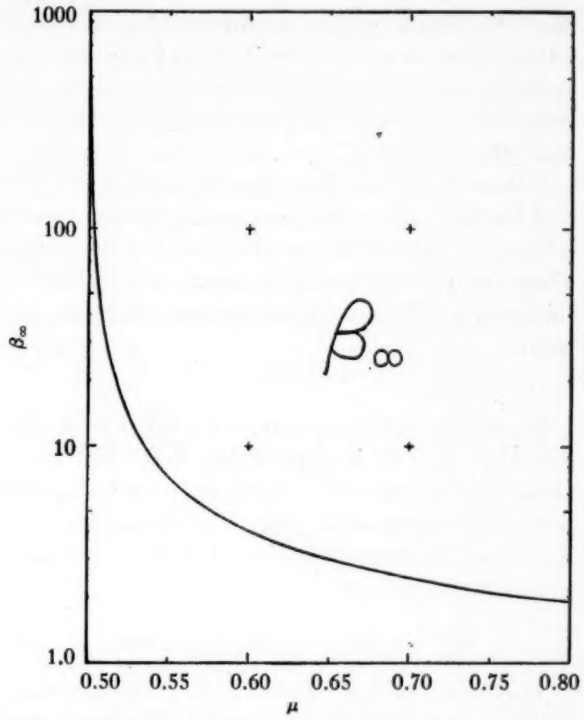

FIG. 3. The approximation constant β_∞ as a function of μ.

The total solubility in terms of volume fraction of rubber is therefore

$$\phi_r=\sum \phi_i=\int_0^\infty v_r f(m)dm/(v_s+v_p e^{Am}). \quad (22)$$

Equation (22), while rigorously correct is not very helpful when it comes to actual calculation. Given the distribution function $f(m)$, either explicitly or graphically, the ratio of v_r to v_0 and the value of μ for the mixture, one can make the calculation, for v_s and v_p are functions of the above variables—but the computation may be exceedingly long and tedious.

Exact calculation of A is extremely difficult, since both ϕ_0 and ϕ_0' are functions not only of $\bar{m}_N$ and $\bar{m}_N'$ but also of the distribution function itself. It is to be noted, however, that the values of ϕ_r (i.e., $1-\phi_0'$), calculated for various m's, approach the limiting curve for $m=\infty$ asymptotically as μ increases. Hence, for values of μ sufficiently above the critical point, one may take for A, the value A_∞ calculated for $m=\infty$. For $m=\infty$, $\phi_0=1$, since the rubber is completely insoluble above the critical point, so that

$$A_\infty=\mu(\phi_r')_{m=\infty}+\ln[1-(\phi_r')_{m=\infty}]. \quad (23)$$

Since, when $m=\infty$ in Eq. (1) $(\phi_r')_{m=\infty}$ is a function of μ alone:

$$\ln[1-(\phi_r')_{m=\infty}]+(\phi_r')_{m=\infty}+\mu(\phi_r')^2_{m=\infty}=0, \quad (24)$$

one may calculate A_∞ as a function of μ. The results of these calculations are shown graphically in Fig. 2. Actually, these calculations of A are accurate virtually to the critical point, thanks to compensating errors.

Certain other approximations may also be made: For dilute solutions, where the swollen rubber phase is small in comparison to the solution, v_s may be taken as approximately equal to v_0, the amount of solvent added.

Further, one may write v_p as a function of the amount of rubber in the precipitate, v_r' and the percentage of the precipitate which is rubber, ϕ_r'.

$$v_p=v_r'/\phi_r'=v_r'/(1-\phi_0'), \quad (25)$$

and hence the solubility

$$\phi_r=\int_0^\infty \frac{v_r f(m)dm}{v_0+(v_r'/\phi_r')\exp(Am_i)}. \quad (26)$$

We may, however, determine an approximate limiting value of ϕ_r' by taking the value for

$\bar{m}_N = \infty$, which is the asymptote for all finite values of $\bar{m}_N$ as μ increases. The asymptotic value $1/(\phi_r')_{m=\infty}$, which we shall henceforth call β_∞ is a function of μ only, and may be calculated from Eq. (24).

Values of β_∞ are shown graphically in Fig. 3.

A further approximation may be made in cases where μ is appreciably greater than the critical μ_c. Then the solubility will be small and nearly all the rubber will be in the precipitate, and one may write

$$v_r' \cong v_r. \tag{27}$$

Nearer the critical point, the solubility is considerable, and v_r' is appreciably smaller than v_r. Here also, however, ϕ_r' is less than $(\phi_r')_{m=\infty}$, and partially compensates. Since this deviation of ϕ_r is not usually as marked[11] as that of v_r, one may say as a general rule

$$\beta v_r' = v_r'/\phi_r' \leqq v_r/(\phi_r')_{m=\infty} = \beta_\infty v_r. \tag{28}$$

Therefore one may write as a final approximate form for the solubility

$$\phi_r \cong \int_0^\infty \frac{f(m)dm}{(v_0/v_r)+\beta_\infty \exp(A_\infty m)}. \tag{29}$$

Because of the condition of Eq. (28), one will expect that the actual solubility will be greater than that calculated from Eq. (29). Errors in determining A are distinctly second order compared to those involving β.

B. Solubility of "Gel" Rubbers

One further point must be noted—Eq. (29) as it stands applies only to rubber which is 100 percent soluble in "good" solvents ($\mu < 0.50$)—the so-called "sol rubber." Actually much rubber consists of more or less highly cross-linked material which is completely insoluble in all solvents—the so-called "gel rubber"—all vulcanized rubber is of this type. This gel can swell greatly so that the rubber phase may be very voluminous, but none of the cross-linked material will be found in the solution phase.

This swelling may be calculated, as was shown by Flory and Rehner.[12] By assuming the cross-linked gel to be an infinite three-dimensional network of chains and deriving a suitable expression for the entropy of elastic stretching, they obtain, as the condition for swelling equilibrium

$$\ln(1-\phi_r)+\phi_r+\mu\phi_r^2+\frac{\rho_r V_0 \phi_r^{\frac{1}{3}}}{M_c}=0, \tag{30}$$

where V_0 = molecular volume of solvent; ρ_r = density of rubber; M_c = average molecular weight of chains between cross links.

For gels which are not highly cross-linked, M_c is very large (of the order of 100,000) and the last term of Eq. (30) is negligibly small. If this last term is neglected, the equation is identical with Eq. (18). Hence for loosely cross-linked networks, such as found in unvulcanized rubbers, the degree of swelling may be taken as roughly the same as that of the sol for the range in which we are interested.[13]

We may therefore write as the generalized case:

$$\phi_r \cong K\int_0^\infty \frac{f(m)dm}{(v_0/v_r)+\beta e^{Am}}, \tag{31}$$

where K is the fraction of the rubber which is "sol."

The solubility may also be expressed as the fraction of the rubber dissolved, S. In this case one may write

$$S = \text{fraction dissolved} = \frac{\phi_r v_s}{v_r}$$

$$\cong K\int_0^\infty \frac{f(m)dm}{1+(v_r/v_0)\beta e^{Am}}. \tag{32}$$

C. Fractionation

(1) *Methods of Fractionation*

For a long time, at least two different methods have been in general use for fractionation of high polymers:

(*a*) *Precipitation method.*—The raw polymer is dissolved in a good solvent, and then successive amounts of a non-solvent are added to the solution, producing fractional precipitation. The highest molecular weights are the first to precipitate, then the next highest, and so forth.

[11] It can be shown mathematically that, even at the critical point, ϕ_r' is greater than $\frac{1}{3}(\phi_r')_{m=\infty}$. Hence $\beta_\infty < \beta < 3\beta_\infty$.

[12] P. J. Flory and J. Rehner, J. Chem. Phys. 11, 521 (1943).

[13] For lower values of μ (below 0.50), the sol is completely soluble, but the gel is never soluble.

(*b*) *Extraction method.*—The raw polymer is successively extracted with mixtures of a good solvent and a non-solvent, increasing the relative proportion of solvent with each extraction. In this case, the lowest molecular weights are extracted first, and then higher molecular weights and so on.

Both of these methods can be interpreted in terms of the same theory, based essentially on Eq. (15). In both cases, each step consists of the establishment of thermodynamic equilibrium between a swollen rubber phase and a solution containing varying quantities of solvent and non-solvent.

(*2*) *Theory of Fractionation*

In a polymer of a given distribution $f(m)$ (Eq. (19)), the equilibrium distribution of any fraction of molecular weight m between solution and precipitate phase is expressed by Eq. (15).

We may then develop equations in a similar manner as before. The actual amounts of the ith fraction in each phase w_i (solution) and w_i' may be written as

$$v_i=\phi_i v_s+\phi_i' v_p=w_i+w_i'; \tag{33}$$

$$w_i'/w_i=\phi_i' v_p/\phi_i v_s=(v_p/v_s)\exp(Am_i). \tag{34}$$

Solving Eqs. (33) and (34) for w_i and w_i' and utilizing the approximations of Eq. (29)

$$w_i'=\frac{v_i}{1+(v_s/v_p)\exp(-Am_i)} \cong \frac{v_i}{1+(v_0/v_r'\beta)\exp(-Am_i)}; \tag{35}$$

$$w_i=\frac{v_i}{1+(v_p/v_s)\exp(Am_i)} \cong \frac{v_i}{1+(v_r'/v_0)\beta\exp(Am_i)}. \tag{36}$$

In all our further considerations, we shall assume that the solvent-non-solvent mixture may be considered as a homogeneous liquid, the same in both phases,[14] and with an interaction with the rubber characterized by a μ_m calculated from Eq. (44) of Part I.

From this μ_m, which depends on the relative proportions of solvent and non-solvent, one may calculate A and β as before. v_r'/v_0 is nothing more than the concentration c (in units of volume fraction) of the precipitated rubber in the total mixture.

We may therefore express the distribution functions of the rubber in the solution and in the precipitate as follows:

Precipitate:

$$f_p(m_i)=[f(m_i)]/1+[\exp(-Am_i)]/\beta c, \tag{37}$$

Solution:

$$f_s(m_i)=[f(m_i)]/[1+\beta c\exp(Am_i)], \tag{38}$$

where of course:

$$f_p(m_i)+f_s(m_i)=f(m_i). \tag{39}$$

The actual amounts in precipitate and solution are therefore:

$$w_p=v_r\int_0^\infty \frac{f(m)dm}{1+(e^{-Am})/\beta c}, \tag{40}$$

$$w_s=v_r\int_0^\infty \frac{f(m)dm}{1+\beta c e^{Am}}. \tag{41}$$

It is apparent immediately[15] from the above equation that in any such distribution of the rubber between the two phases, most of the high molecular weight material will be in the precipitate, and most of the low molecular weight material in the solution. There is no sharp division since there will be some of every fraction in both phases. In the case of the high molecular weights, the amount in the solution may well be negligible since

$$\lim_{m\to\infty} 1/(1+\beta c e^{Am})=0, \tag{42}$$

but there will always be at least βc of the low molecular weight material in the precipitate,

[14] This is not strictly true, for the solution will actually be slightly richer in non-solvent and the precipitate in solvent, but treatment of such a condition leads to tremendous complications, and the above assumptions seem to introduce no errors of great significance, when compared with unpublished experimental results of the author.

[15] All of the following qualitative conclusions are quite rigorous. Actually Eqs. (40) and (41) are precise until one makes simplifying assumptions in order to calculate β and A. The dependence on molecular weight is quite accurate, however.

since

$$\lim_{m\to 0}\frac{1}{1+(e^{-Am}/\beta c)}=\frac{\beta c}{1+\beta c}=\frac{v_p}{v_p+v_s}\leqq\beta c. \quad (43)$$

This last fact is important, for in the precipitation method of fractionation, a finite amount of the low molecular weight material will always be in the precipitate, a fact which is well known empirically. That this should be is to be seen from a consideration of the interaction between the molecules. If the interaction between the rubber molecule and the solvent is the same as the interaction between it and the rest of the rubber, then it is completely indifferent as to its distribution, in which case, its concentration will be the same in both phases. In general however, the rubber molecule interacts more strongly with molecules of its own kind than with the solvent (and more so with increasing discrepancies between the molecular weights of rubber and solvent); and therefore the concentration in the rubber phase, even of the lowest molecular weight fractions, will always be higher than that in the solution phase, which is essentially solvent.

As indicated above, this is a purely thermodynamic effect, and is not caused by mechanical co-precipitation or occlusion as has been suggested in the past.

With increasing values of μ, A increases,[16] so that the tendency for the rubber to be in the precipitate phase increases; hence one obtains fractionation by systematically varying μ in one direction or the other, taking advantage of the fact that the distribution between the two phases is strongly dependent on the molecular weight.

(3) *Comparison of the Precipitation and Extraction Methods*

It is now desirable to consider more in detail the two different methods of fractionation.

In the precipitation method, the polymer is dissolved in a good solvent and then small increments of a non-solvent or precipitant (such as methyl alcohol) added until the solution breaks into two phases, with the formation of a swollen rubber phase or precipitate. This, of course, cannot occur until sufficient of the non-solvent is added to increase μ_m beyond the critical value defined by Eq. (6).

The original rubber of distribution function $f(m)$ has now distributed itself between the two phases, and the distributions in the two phases are defined by $f_p(m)$ and $f_s(m)$ in Eqs. (37) and (38). The solution is then decanted and fractionation continued on it by adding more non-solvent and so increasing μ_m further. Two phases exist again, with similar equations holding:

$$f_s'(m)=\frac{f_s(m)}{1+\beta' c\exp(A'm)}=\frac{f(m)}{(1+\beta' c' e^{A'm})(1+\beta c e^{Am})}; \quad (44)$$

$$f_p'(m)=\frac{f_s(m)}{1+[\exp(-A'm)]/\beta' c}=\frac{f(m)}{\{1+[\exp(-A'm)]/\beta' c\}\{1+\beta c e^{Am}\}}. \quad (45)$$

More generally one may express the distribution in the nth fraction as:

$$f_s^n(m)=\frac{f(m)}{(1+\beta_a c\exp(A_a m))(1+\beta_b c\exp(A_b m))\cdots(1+\beta_n c\exp(A_n m))}; \quad (46)$$

$$f_p^n(m)=\frac{f(m)}{(1+\beta_a c\exp(A_a m))(1+\beta_b c\exp(A_b m))\cdots\left(1+\frac{\exp(-A_n m)}{\beta_n c}\right)}. \quad (47)$$

The distribution function of the nth fraction is therefore represented by $f_p^n(m)$. Actually, this may be very nearly represented by neglecting all but the last two terms in the denominator.

$$f_p^n(m)\cong\frac{f(m)}{(1+\beta_m c\exp(A_m m)\left(1+\frac{\exp(-A_n m)}{\beta_n c}\right)}. \quad (48)$$

This function starts out at a very small value

[16] β decreases with increasing μ, but this is more than offset by the increase in A.

for $m=0$, increases to a maximum and then decreases to zero for $m=\infty$.

$$\lim_{m\to 0}\frac{1}{(1+\beta_m c\exp(A_m m))\left(1+\dfrac{\exp(-A_n m)}{\beta_n c}\right)}=\frac{\beta_n c}{(1+\beta_m c)(1+\beta_n c)}\cong\beta_n c; \quad (49)$$

$$\lim_{m\to\infty}\frac{1}{(1+\beta_m c\exp(A_m m))\left(1+\dfrac{\exp(-A_n m)}{\beta_n c}\right)}=0. \quad (50)$$

In the extraction method, the polymer is extracted with a blend of solvent and non-solvent, such that a small fraction of the total polymer—largely low molecular weight material—is removed. Here again the distribution between the solution and the swollen rubber is defined by Eqs. (37) and (38). The solution is decanted, and the precipitate is further fractionated by extraction with a solvent mixture of lower μ_m.

The following two items are the two essential differences in the two methods: (1) In the precipitation method, μ is systematically increased; in the extraction method, μ is systematically decreased. (2) In the precipitation method, the fraction removed is in the precipitate, and the solution is further fractionated while in the extraction method, the fraction removed is in the solution, and the precipitate is further fractionated.

Following the same line of reasoning as in Eqs. (44) to (47), except in the reverse direction, one finds that for the mth fraction, in the case of the extraction method

$$f_s^m(m)=\frac{f(m)}{\left(1+\dfrac{\exp(-A_z m)}{\beta_z c}\right)\left(1+\dfrac{\exp(-A_y m)}{\beta_y c}\right)\cdots(1+\beta_m c\exp(A_m m))}; \quad (51)$$

$$f_p^m(m)=\frac{f(m)}{\left(1+\dfrac{\exp(-A_z m)}{\beta_z c}\right)\left(1+\dfrac{\exp(-A_y m)}{\beta_y c}\right)\cdots\left(1+\dfrac{\exp(-A_m m)}{\beta_m c}\right)}. \quad (52)$$

The distribution function for this fraction is therefore represented by $f_s^m(m)$ which may be closely represented by

$$f_s^m(m)\cong\frac{f(m)}{(1+\beta_m c\exp(A_m m))\left(1+\dfrac{\exp(-A_n m)}{\beta_n c}\right)}. \quad (53)$$

It is to be seen that to this degree of approximation, this fraction of the extraction method has the same distribution as the nth fraction in the precipitation method, since Eq. (53) is the same as Eq. (48).

We may therefore say that, to the first approximation, the results of the two methods are identical, and that essentially the same fractions are obtained in both ways.

This is not exactly true, however, for the exact Eqs. (47) and (51) are not identical. In the first place, A and β are actually dependent on the actual distributions in the mixture, which are quite different for the two methods. Therefore

$$(A_m)_{\text{extraction}}\neq(A_m)_{\text{precipitation}}; \quad (54)$$

$$(\beta_m)_{\text{extraction}}\neq(\beta_m)_{\text{precipitation}}. \quad (55)$$

This of course will introduce differences, but this effect is distinctly secondary compared with a second factor which we may call the tail effect.

If we take the limiting cases of Eqs. (47) and (51) for low molecular weights, we find that

Precipitation:

$$\lim_{m\to 0} f_p^n(m)=\frac{\beta_n c}{(1+\beta_a c)\cdots(1+\beta_n c)}; \quad (56)$$

Extraction:

$$\lim_{m\to 0} f_s^m(m) = \frac{(\beta_n c)\cdots(\beta_z c)}{(1+\beta_n c)\cdots(1+\beta_z c)}. \qquad (57)$$

Hence, we see that since $\beta c \ll 1$ the most significant difference is that in the extraction method, far less low molecular weight material will be found in the higher fractions than is the case for the precipitation method.

It would seem therefore that, normally, the extraction method of fractionation should be preferable to the precipitation method. Certain objections to such a choice might be raised:

(1) Because of the large and compact nature of the rubber phase, equilibrium is reached much more slowly in the extraction method.

(2) If insoluble gel is present, its great swelling will cause a tremendous overlapping in the higher fractions.

(3) Because of the great sensitivity of the solubility to slight changes in μ, it is very difficult to choose solvent mixtures properly in the extraction method.

It remains for the individual investigator to choose between the methods. In the opinion of the author, the precipitation method, if modified to the extent of washing the precipitate or reprecipitating the fraction (in order to remove the "tail"), is adequate for all ordinary purposes.

(4) *Effect of Temperature*

The temperature has no effect upon the general considerations of fractionation in the preceding pages. However, since μ is known both theoretically and experimentally, to be a function of temperature, decreasing as T increases,[17] it follows that the temperature is involved in any fractionation in practice. In general, during the process of fractionation, by either method, the temperature should be kept relatively constant or anomalous results may be found.

A variation of the precipitation method is that of inducing precipitation by cooling. Since μ increases with decreasing temperatures, this is thoroughly consistent with the theory developed above.

[17] See Eq. (5), and for further discussion of the dependence of μ on various factors, see M. L. Huggins, Ann. Acad. Sci. **44**, 431 (1943).

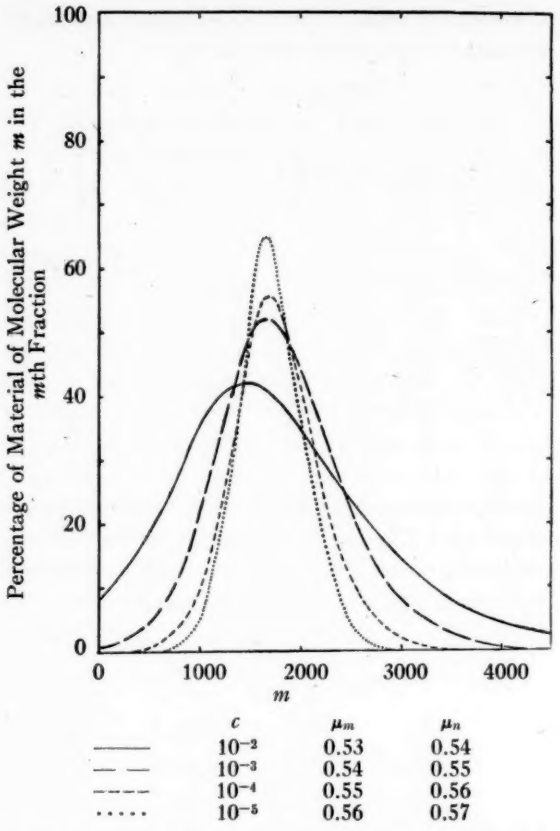

FIG. 4. The effect of concentration on the sharpness of concentration.

(5) *Effect of Concentration*

The influence of concentration is illustrated most effectively by the approximate Eqs. (48) (53). If this function is plotted against c, the "concentration" of the fraction[18]

$$c = v_r'/v_0, \qquad (58)$$

the curves of Fig. 4 result. The curves represent the percentage of material of molecular weight m in a fraction taken between μ_m and $(\mu_m+.01)$, for four different concentrations, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}, the values of μ chosen so that the maximum for each concentration lies in approximately the same range.

[18] This term "concentration" is a trifle unclear. It is the volume of the *rubber* in the *precipitate* as compared with the total *solution*. If, for example, one is fractionally precipitating a 1 percent solution of polymer into ten equal fractions, each fraction is 0.1 percent and $c=0.001$. In the case of the extraction method, c varies in the course of the extraction, since, at the beginning of fractionation, the precipitate phase contains the whole polymer.

Figure 4 shows that there are two factors involved in varying c.

(a) For smaller values of c, the fractionation is sharper; there is less "tail" effect, and the maximum is higher.[19] Had a fraction in the lower molecular weight range been chosen, the curve would have been still sharper.

(b) With higher dilutions, that is, smaller values of c, the value of μ necessary for precipitation of a given fraction is greater. For example, a dilution of 10-fold requires an increase of μ_n (and μ_m) by 0.01 unit. In the case of the lowest fractions, this shift is more appreciable.

From the foregoing discussion it is clear that from a theoretical point of view, c should be kept as small as possible to obtain the sharpest fractionation. Practically, however, one cannot carry such a solution too far. Not only does this entail working with great quantities of solution, but, because of the shift of μ with concentration, it may be next to impossible to separate the lowest fractions without adding tremendous quantities of precipitant.[20]

[19] The fact that the maxima in Fig. 4 correspond to only about 60 percent of the material of $m=1700$ ($MW=170{,}000$) is not significant. Had a wider range been taken (i.e., $\mu_n-\mu_m=0.02$), such that the fraction was larger, the maxima would have approached 100.

[20] It would seem that, since the lowest fractions are fairly sharp, even when precipitated from a concentrated solution, the best procedure would be to start fractionation in a very dilute solution, but after separation of the higher fractions, to concentrate the material to facilitate separation of the lower fractions. This is, however, a complicated procedure.

In practice, one must strike a compromise. Most fractionations are carried out from solutions where the initial concentration of the total polymer is about 1 percent. For a fractionation into ten equal fractions, this corresponds roughly to $c=10^{-3}$. This seems to give fairly good results, judging both from the experimental results, and from the $c=10^{-3}$ curve in Fig. 4.

(6) *Effectiveness of Fractionation*

Some idea of the effectiveness of fractionation can be seen from Fig. 4. The distribution of each fraction is fairly broad especially for fractionation carried out at high concentrations. Especially objectionable is the "tail" effect, for the presence of even a small amount of low molecular weight material can alter the number average molecular weight appreciably.

A better fractionation can be obtained either by refractionating or by washing the precipitate with a fresh sample of the precipitating mixture; either procedure serves to remove the lowest subfractions, while not materially affecting the rest of the fraction. This solution may then be added to the decanted supernatant solution and fractionation continued. Experiments show that these methods are reasonably effective in eliminating the "tail."

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The Influence of Molecular Flexibility on the Intrinsic Viscosity, Sedimentation, and Diffusion of High Polymers*

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Expressions for the mean square separation of chain ends and modifications of the formula for an ideal coil are discussed. On the basis of these and of the hydrodynamic theory of intrinsic viscosity, an interpretation of the modified Staudinger rule is offered. It relates the exponent a of the molecular weight to a flexibility parameter p of the chain in a given solvent, varying between zero and one (Eq. (4), (5)). Recent data on polystyrene and on cellulose nitrate are analyzed in greater detail. By means of the frictional ratio f/f_0, the sedimentation constant s and the diffusion constant D, respectively, are connected with the degree of polymerization in terms of p (Eq. (9)). The limiting dependence of sedimentation and diffusion rate upon molecular weight for a straight chain and an ideal coil is also found in this manner. A comparison shows satisfactory agreement between values for p found from intrinsic viscosity and those determined from sedimentation or diffusion rates, for certain cellulose esters and starch derivatives. Effects of solvent and of inhomogeneity in respect to molecular weight are discussed briefly.

INTRODUCTION

THE physical methods employed to determine molecular weights of high polymers in solution are based either on the measurement of a colligative property like osmotic pressure or sedimentation equilibrium, or a rate phenomenon, such as the viscosity increment due to the solute or the rates of sedimentation and diffusion of the solute. The second type of procedure is more easily applicable from the experimental point of view, while its interpretation is more involved than that of measurements of the former type. The determination of polymerization degrees from viscosity data is based on Staudinger's empirical rule or a modification thereof obtained by calibration of the procedure by means of an absolute method. In this way an empirical relation is obtained between the intrinsic viscosity and the molecular weight. In the case of sedimentation-diffusion, an expression for the molecular weight is derived in a straightforward way. For polydisperse systems however, it is not immediately evident what type of molecular weight average results.

Present theories on the other hand, establish relations between the intrinsic viscosity and the shape of the solute molecule.[1] Similarly, the result of a sedimentation-diffusion measurement can be related to the shape of the sedimenting particle by means of the so-called frictional ratio.[2] A connecting link between some of the empirical results in terms of molecular weight and present theories can be established, if the shape of long chain molecules in solution can be related to their degree of polymerization. In this manner it becomes possible also to relate the intrinsic viscosity and the molecular weight to the individual sedimentation or diffusion constants instead of their ratios only. It is the purpose of this article to examine certain aspects of these questions.

I. SHAPE OF LONG CHAIN MOLECULES IN SOLUTION

It has been shown by various authors[3] following Rayleigh's[4] treatment of the problem of random flight, that the mean square separation of ends in a chain consisting of N freely rotating links is given by

$$\lim_{N\to\infty} \langle R^2\rangle_{Av} = AN, \tag{1}$$

where A is the squared length of a link and R the

* Publication assisted by The Graduate School of Howard University.

[1] See for instance R. Simha, J. App. Phys. **13**, 147 (1942).

[2] *The Ultracentrifuge*, Ed. The Svedberg and Kai O. Pedersen (Oxford University Press, New York, 1940).

[3] W. Kuhn, Kolloid Zeits. **68**, 2 (1934); E. Guth and H. Mark, Monats. **65**, 93 (1934).

[4] Compare the excellent discussion by S. Chandrasekhar, Rev. Mod. Phys. **15**, 2 (1943).

distance between chain ends. The constancy of the valence angle merely introduces a numerical factor. Relation (1) will remain valid also if an energy barrier to rotation exists, provided that rotational symmetry is preserved (ethane-type of barrier). The factor A is modified and becomes a function of the height of the energy hump and of the temperature.[5] Equation (1) can be generalized. If a distribution of "step" lengths,

$$\tau(x, y, z)dxdydz,$$

exists in proceeding from the ith joint to the $(i+1)$th, and τ is independent of the ordinal number i, where x, y, z denotes a set of coordinates through the joint, one obtains[4]

$$\lim_{N\to\infty} \langle R^2\rangle_{Av} = AN + BN^2. \qquad (1a)$$

A indicates the mean square of the length of a "step" or effective length of a link, averaged over the distribution τ. B denotes the sum of the squares of the mean displacements in 3 directions

$$B = \langle\xi\rangle^2 + \langle\eta\rangle^2 + \langle\zeta\rangle^2.$$

The system ξ, η, ζ results from the original one by means of a certain orthogonal transformation which need not be specified here. If the function τ possesses the previously mentioned symmetry properties, $B=0$. Thus again a random distribution of chain end distances is obtained, however superimposed upon that resulting from a straight extension of the chain. B is a measure of the geometrical anisotropy existing in the structure.

Considering now an actual chain molecule, the fact that "tracing back of steps" or back coiling of the chain is restricted because of the space filling effect of the substituents, requires a modification of the considerations leading to relation (1). It is extremely difficult to evaluate this effect in detail, since the direction of each successive link now becomes dependent upon that of the preceding one. However, it may be seen that, on the average, a straightening out of the chain coil will occur, larger values of the separation of chain ends, than in the ideal case, being more probable. The actual chain may therefore be replaced in a first approximation by one in which there exists a distribution τ of displacements around each joint, and independent of its position within the molecule, giving rise to a mean value $\langle R^2\rangle_{Av}$ as in (1a). For the large degrees of polymerization involved, even slight deviations from symmetry can lead to appreciable values for the second term in (1a). Unless the range of N-values is large, this equation can be approximately replaced by a single term with an intermediate exponent, thus

$$\langle R^2\rangle_{Av} = CN^{1+x}; \quad 0<x<1, \qquad (1b)$$

C is a constant. $x=0$ corresponds to the ideal coil, as defined in (1), $x=1$ to a straight chain. Thus we arrive at a result similar to the one suggested previously by Kuhn.[3] It may be noted that in the transition from (1a) to (1b), x increases with B while C decreases. For $N\approx 10^3$, a value of x of 0.4–0.5 can increase the value of $(\langle R^2\rangle_{Av})^{\frac{1}{2}}$ for a paraffin chain by a factor of several units. Finally the influence of the solvent must be taken into account. Stuart's[6] experiments on models propose to reproduce the difference between an inert and a good solvent. In the latter system the chains are straightened out. The solvent in this instance prevents the polymer molecule from curling up. This may be due in part to actual solvation and in part may be considered analogous to the conditions which prevent the formation of a drop and lead to spreading of a film. As is well known,[7] this occurs when the energy of adhesion between upper and lower liquid exceeds the cohesion within the former one. Of course, in our case, the entropy factor is the primary source for the tendency in the single polymer molecule to form a "drop." Furthermore these considerations can apply to dilute solutions only.

II. INTRINSIC VISCOSITY, MOLECULAR WEIGHT, AND DIMENSIONS

Since Staudinger first proposed his relation, it has become necessary to modify it. For relatively small molecular weights, not exceeding 30,000 as a weight average, addition of a constant term[8] has been found satisfactory. For larger molecular

[5] S. E. Bresler and J. I. Frenkel, Acta Physicochimica, U.S.S.R. **11**, 485 (1939).

[6] H. A. Stuart, Naturwiss. **31**, 123 (1943).

[7] Compare for instance N. K. Adam. *The Chemistry and Physics of Surfaces* (Oxford University Press, New York, 1941).

[8] R. Fordyce and H. Hibbert, J. Am. Chem. Soc. **61**, 1912 (1939); P. J. Flory and P. B. Stickney, J. Am. Chem. Soc. **62**, 3032 (1940); W. O. Baker, C. S. Fuller and J. H. Heiss, Jr., J. Am. Chem. Soc. **63**, 3316 (1941).

weights, in accordance with Houwink,[9] the following equation has been applied

$$\eta_i = KM^a = K'Z^a, \qquad (2)$$

where η_i is the intrinsic viscosity, found by extrapolation from a plot of η_{sp}/c *vs.* c. M is the molecular weight of the fraction as determined by an absolute method, Z the degree of polymerization. Since the partial specific volume of the polymer is almost always practically independent of molecular weight, the result remains unaltered if c is expressed as a volume ratio rather than a ratio of weight to volume. A few examples are presented in Table I. The molecular weights were determined partly from osmotic pressure and partly from ultracentrifuge data. In several cases only three points were available for computing a. The homogeneity of the samples varied, those investigated by Mosimann and Gralén being quite inhomogenous. The meaning of the last column is discussed later on. This table is by no means complete. However, it seems to indicate that the exponent a lies roughly between 0.5 and 1.5. It may be noted that relatively slight inaccuracies in the viscosities or molecular weights can produce noticeable variations in a.

As mentioned before, present hydrodynamic theories of intrinsic viscosity introduce as fundamental parameter the shape of the solute molecule.[1,10] If it is approximated by an ellipsoid of revolution, the length-thickness ratio l/d appears in the final result.[1] For the case of overwhelming Brownian motion in the viscosimeter, η_i becomes a rather complicated function of l/d, which has been evaluated in the range between $l/d=1$ and 300.[11] Using these data, Kraemer[12] has given an interpolation formula in the form of a polynomial. However, a simpler equation can be given, which is more useful for our purposes, namely:

$$\left.\begin{aligned} &\eta_i \approx 0.233(l/d)^{1.698}; \quad 20 \leqq l/d \leqq 100; \\ &\qquad \text{Average deviation 1.2 percent} \\ &\eta_i \approx 0.207(l/d)^{1.732}; \quad 20 \leqq l/d \leqq 300; \\ &\qquad \text{Average deviation 2.3 percent} \end{aligned}\right\} \qquad (3)$$

[9] R. Houwink, J. prakt. Chem. **157**, 15 (1940).

[10] W. Kuhn, Helv. Chim. Acta **26**, 1394 (1943), where previous references are given. In the present author's opinion, Kuhn's hydrodynamic treatment and others derived therefrom, contains an incorrect assumption for the limit of vanishing shear gradient, which makes the result for η_i too small. See R. Simha, J. Phys. Chem. **44**, 25 (1940).

[11] J. W. Mehl, J. L. Oncley and R. Simha, Science **82**, 132 (1940).

[12] E. O. Kraemer, J. Frank. Inst. **231**, 1 (1941).

TABLE I.

Solute	Solvent	a	p
Polyisobutylene	Diisobutylene	0.64[a]	0.38
Polystyrene (polymerization temperature 60°C)	Toluene	0.70[b]	0.42
Polystyrene, 120°C	Toluene	0.81[b]	0.47
Polystyrene, 180°C	Toluene	1.14[b]	0.68
Cellulose	Schweitzer's reagent	0.80[c]	0.47
Amylose acetate	Methyl acetate	0.95[d]	0.57
Cellulose acetate	Acetone	1.0[e]	0.59
Cellulose nitrate	Acetone	1.0[f]	0.60
Polyvinyl chloride	Cyclohexanone	1.0[g]	0.59
Amylose	Ethylene diamine	1.5[h]	0.88

[a] P. J. Flory, J. Am. Chem. Soc. **65**, 372 (1943).
[b] See reference 15.
[c] See reference 19.
[d] See reference 22.
[e] M. Harris and A. Sookne, private communication. Molecular weights from osmotic pressure.
[f] See reference 18.
[g] D. J. Mead and R. M. Fuoss, J. Am. Chem. Soc. **64**, 277 (1942).
[h] J. F. Foster and R. M. Hixon, J. Am. Chem. Soc. **66**, 557 (1944).

With increasing axis ratio, the exponents increase slowly but do not reach a value of two within the range of importance. For smaller values of l/d, the exponent in (3) assumes a value of 1.72, the factor equals 0.217, and a constant equal to 2.283 is to be added, similarly as in the correction to Staudinger's rule.[8] η_i is expressed in terms of volume concentration. The axis ratios computed from measured viscosities represent the dimensions of the effective ellipsoid which makes the same contribution to η_i as the actual molecule. This is certainly not more than a rough approximation. For high degrees of polymerization, where the chains form preferentially compact coils,[10] this should be more satisfactory than for intermediate ones. For short chains on the other hand, where curling up is insignificant, this approximation should again be more adequate. However in the following, we shall be concerned only with the former extreme. Furthermore, the possibility of solvation in good solvents contributing to the observed large intrinsic viscosities has been disregarded and the whole effect attributed to the asymmetry of the unsolvated structure. In the case of globular proteins, it has been possible to discriminate to some extent between these two possibilities by comparison of viscosity and diffusion-sedimentation data.[11] The difficulties encountered at present in the evaluation of such measurements for chain polymer systems, make this possibility appear doubtful in our cases. However, for high asymmetries, the solvation effect can produce only errors which

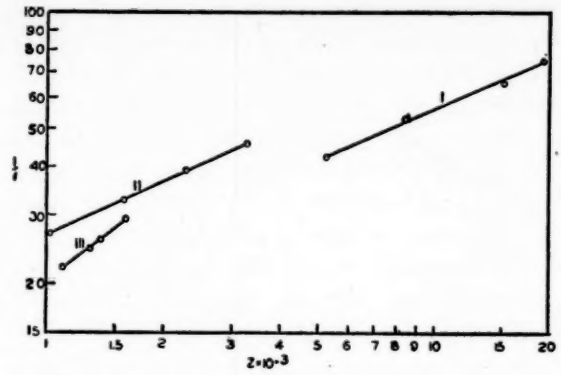

FIG. 1. Double logarithmic plot of asymmetries l/d *vs.* degree of polymerization Z for polystyrene:
I Polymerization temperature 60°C.
II Polymerization temperature 120°C.
III Polymerization temperature 180°C.

are minor compared with those arising from other difficulties. In our applications two further points must be kept in mind. First the fact, that for a given degree of polymerization, the length and diagonal dimensions are only statistically defined. Therefore Eq. (3) must be modified to contain $\langle (l/d)^q \rangle_{Av}$, where q is the exponent in (3) and the average is formed over the distribution of dimensions in the coil in solution. The exact form of this distribution is not known except for idealized cases, in which expressions of an essentially Gaussian type are obtained.[4] However, the above average will differ from $\langle (l/d)^2 \rangle^{q/2}_{Av}$ only by a numerical factor of the order of unity. Secondly, the polydispersity of the solute must be taken into account. The mean axis ratio determined from the intrinsic viscosity of a mixture is:

$$\langle l/d \rangle_{Av} = \{ \sum_i (l/d)_i W_i \}^{1/q},$$

where W_i is the weight fraction of species i with axis ratio $(l/d)_i$ in the mixture. The higher the molecular asymmetry, the greater the effect of inhomogeneity.[12]

To provide, with these reservations, a bridge between Eqs. (2) and (3), the dimensions of the polymer molecule must be expressed as a function of the degree of polymerization. It is not difficult to obtain the result in two limiting cases, namely those of a perfectly straight chain and an ideal flexible coil respectively. In the first instance, the longest dimension increases proportionally to the molecular weight, the cross section remains constant in a homologous series, and the axis ratio is therefore proportional to Z. In the other extreme, the mean separation of chain ends is given by relation (1). Kuhn[3] has shown that in such a structure on the average all dimensions increase at the same rate with the molecular weight. Thus the axis ratio becomes independent of the degree of polymerization. Our previous considerations in Part I lead for a chain in solution to an equation of type (1b), corresponding to a certain anisotropy of the structure. We may therefore expect an expression,[1]

$$l/d = CZ^p; \quad 0 < p < 1, \tag{4}$$

to hold approximately. The lower limit of the exponent characterizes the ideal coil, the upper one a straight rigid chain. Combination of Eqs. (4) and (3) leads directly to the empirical formula (2) with

$$a \doteqdot 1.7p. \tag{5}$$

In this manner most of the values in the last column of Table I were computed, with the exception of the values for polystyrene and nitrocellulose which were found directly from suitable plots and are slightly different. However (5) is sufficiently accurate for a rapid calculation of p from a or *vice versa*. It follows from (4) and (5), that the maximum possible value of the viscosity exponent a should lie around 1.7. In those cases in which Staudinger's equation holds, a value for p of 0.59 results, approximately halfway between zero and one. According to this theory no particular physical significance is to be attached to the case $a=1$. Furthermore it is understandable for instance, that for polyisobutylene the value lies below that for the cellulose esters. Also it may be expected that for a given polymer, in a poorer solvent or solvent mixture, the p-values will be smaller than in a thermodynamically better one. The behavior of cellulose acetate in acetone-methanol mixtures seems to be in agreement with this conclusion, since p decreases with the addition of methanol.[13] Measurements of the depolarization factor of the light scattered by the particle[14] should also reveal an increased degree of coiling upon addition of precipitant. Furthermore, preferential forward scattering should appear at higher molecular weights in the poorer solvent system.

[13] H. Mark, private communication.
[14] See for instance P. Debye, J. App. Phys. **15**, 338 (1944).

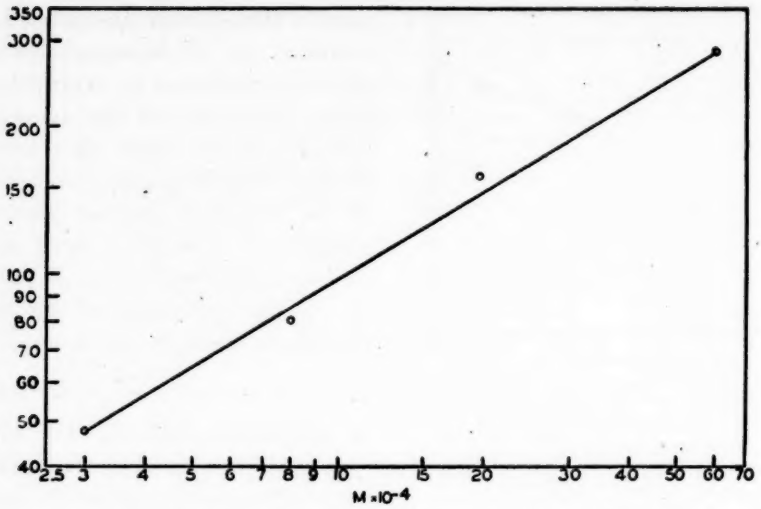

FIG. 2. Double logarithmic plot of asymmetries l/d *vs.* molecular weight M for cellulose nitrate.

Figure 1 gives logarithmic plots of l/d, as determined from viscosity,[10,11] *vs.* Z for the three series of polystyrenes. Equation (4) is satisfied. Tables II–IV contain the experimental data together with the dimensions l and d computed therefrom. No data on the partial specific volumes of the fractions were reported. Therefore a value of 0.93 was assumed for all three series. The third column was computed from Eq. (4). Using a value of 2.5A-units for the monomer, a maximum length l_{max} can be found. l_{max}/l varies in the three series respectively from 15.5 to 9.1, 6.3 to 4.2, and 5.4 to 4.9, indicating degrees of coiling increasing with Z, as is to be expected. An increase of the viscosity exponent a and the flexibility parameter p is accompanied by an increase of the slope of the reduced osmotic pressure curves.[15] According to present theories,[16] this indicates a better solvent, in which a relative straightening out of the chains becomes understandable. On the basis of the fact, that his "constants" K decreased with increasing temperature of polymerization, Staudinger suggested that branching is favored under such conditions. This question can of course not be decided on the basis of viscosity alone. True, the proportionality factors in the equations for l/d decrease between 60° and 180°. However, this may not be more than a consequence of the increase in p, as discussed in connection with Eqs. (1a) and (1b). This increase in p indicates increased stiffening of the chains. Now a branched structure offers more resistance to convolutions of the chain than a linear one. Furthermore the chains become more symmetrical (smaller l/d), for the same degree of polymerization, as may be seen by comparison of the first and last rows in Table IV with the last two in the preceding one. Clearly more measurements on overlapping fractions prepared at different temperatures are needed.[17]

Mosimann's[18] measurements on nitrocellulose were also analyzed. Figure 2 shows plots of $\log l/d$ *vs.* $\log M$. Equation (4) is applicable to the four highest molecular weights, ranging from 613,000 to 30,000. The degrees of nitration are slightly different. The two smallest degrees of polymerization were found by means of equilibrium measurements in the ultracentrifuge, the

TABLE II. Polystyrene 60°.

η_i	Z(obs) $\times 10^{-3}$	Z(calc) $\times 10^{-3}$	l/d	$l \times 10^{-3}$ (A)	d (A)
355	19.7	19.6	75	3.18	42
295	15.2	15.0	67	2.77	41
200	8.6	8.8	53.5	1.95	36
140	5.3	5.2	43	1.45	34

$\eta_i = 3.37 \times 10^{-1} Z^{.70}$; $l/d = 1.17 Z^{.42}$; $l = 7.50 Z^{.61}$; $d = 6.41 Z^{.19}$

[15] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc. **65**, 2319 (1943). I am indebted to Dr. H. Mark for making available the data in more detail than in the publication.

[16] P. J. Flory, J. Chem. Phys. **10**, 51 (1942); M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).

[17] See also M. L. Huggins, J. Am. Chem. Soc. **66**, 1991 (1944).

[18] H. Mosimann, Helv. Chim. Acta **26**, 61 (1943).

remainder from rate data. No inhomogeneity coefficients are given for these samples except for $M=30{,}000$ which had a ratio of 1.65 between weight- and number-average molecular weight. In view of the magnitude of the average axis ratios, ranging from 285 to 47.5, this represents quite high a value. In the original article, values for the molecular asymmetries are presented. They were computed on the basis of theories criticized elsewhere[10] by the present author. A comparison of these l/d-values with the maximum values for a straight chain also shows that they are too large. Using our values for l/d, ratios of l_{max}/l between 2.7 and 1.2 were computed. No detailed analysis of other data presented in Table I was undertaken but merely approximate values of p were computed from Eq. (5).

Equation (4) is based on (1b). For wider ranges of molecular weights in a series, it may be necessary to use a formula modified in accordance with (1a). The Staudinger-type relation (2a) would then be replaced by a corresponding two-term equation.

III. SEDIMENTATION, DIFFUSION, AND MOLECULAR WEIGHT

The basis for the determination of molecular weights from rate measurements in the ultracentrifuge is given by the familiar equation[2]:

$$M=(RT/1-V\rho)\cdot s/D. \tag{6}$$

$(1-V\rho)$ represents the Archimedes-factor, V indicating the partial specific volume of the solute, ρ the density of the solvent. s is the sedimentation constant, D the diffusion constant of the particle. The importance of extrapolating both parameters to zero concentration has been repeatedly emphasized.[18,19] These constants can be related to the shape of the sedimenting particle by means of the frictional ratio f/f_0.[2] It indicates the ratio between the frictional resistance of the actual molecule and a sphere occupying the same volume. If the partial specific volume V of the polymer is independent of the molecular weight, the following equation is obtained:

$$f/f_0=\text{const.}/DM^{\frac{1}{3}}. \tag{7}$$

For an ellipsoidal particle, f/f_0 can be expressed as function of l/d.[20] It has been tabulated up to a value of hundred for the axis ratio,[2] and recently for higher values up to three hundred.[19] Although the original equation is not as cumbersome to evaluate as the viscosity formula, it is again useful for our purposes, to write it as an exponential expression. The interpolation formula:

$$f/f_0\doteqdot 0.506(l/d)^{0.454};\quad 20\leqq l/d\leqq 300;\quad \text{Av. dev. 1.3 percent,} \tag{8}$$

represents the values well.

Axis ratios calculated from the frictional ratios and those obtained from viscosity measurements have been found to agree[11,21] in the case of proteins. The discrepancies become greater for chain polymers, as indicated, for instance, by measurements of Signer and collaborators,[2,1] Gralén,[19] Dombrow and Beckmann[22] and of Mosimann.[18] A comparison of Eqs. (8) and (3) shows that for polydisperse systems, different types of averages for l/d are obtained. Furthermore the molecular weights in (7), if determined from (6), are usually calculated as a ratio of some average sedimentation constant to a weight average diffusion constant, rather than as an average ratio of the two constants. Finally the

TABLE III. Polystyrene 120°.

η_i	Z(obs) $\times10^{-3}$	Z(calc) $\times10^{-3}$	l/d	$l\times10^{-3}$ (A)	d (A)
155	3.3	3.3	46.3	1.29	28
118	2.3	2.3	39.5	1.03	26
86	1.6	1.6	33.0	.82	25
62	1.0	1.1	27.0	.62	23

$\eta_i=2.26\times10^{-1}Z^{.81}$; $l/d=1.02Z^{.47}$; $l=6.83Z^{.65}$; $d=6.72Z^{.18}$

TABLE IV. Polystyrene 180°.

η_i	Z(obs) $\times10^{-3}$	Z(calc) $\times10^{-3}$	l/d	$l\times10^{-3}$ (A)	d (A)
73	1.6	1.6	29.5	.75	26
59	1.4	1.4	26.0	.67	26
53	1.3	1.3	24.5	.62	25
45	1.1	1.1	22.0	.54	25

$\eta_i=1.58\times10^{-2}Z^{1.14}$; $l/d=1.91\times10^{-1}Z^{.68}$; $l=2.25Z^{.79}$; $d=11.74Z^{.11}$

[19] N. Gralén, Thesis, Upsala, 1944. The exponent is calculated from the author's sedimentation-diffusion data in the manner described below.

[20] F. Perrin, J. de phys. et rad. **7**, 1 (1936).

[21] M. A. Lauffer, J. Am. Chem. Soc. **66**, 1188 (1944).

[22] B. A. Dombrow and C. O. Beckmann, private communication. Molecular weights from sedimentation-diffusion.

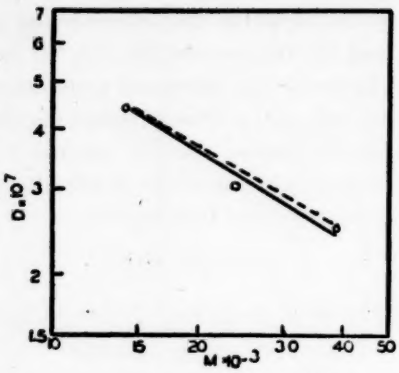

FIG. 3. Double logarithmic plot of diffusion constant D *vs.* molecular weight M for methyl cellulose. Circles indicate experimental values, dashed line the experimental slope, solid line the computed one.

accuracy in determining f/f_0 is limited to a greater extent than that in viscosity measurements, errors up to 20 percent not being out of the ordinary. This makes the above-mentioned discrepancies understandable.

It is assumed now that the particle in the ultracentrifuge has the same l/d-ratio as in the viscosimeter for a given solvent. This should be true for small shear gradients, since the deformation of a flexible coil is a second-order effect.[10] Then it is possible to derive an expression for the separate dependence of the sedimentation or diffusion constant upon the molecular weight from viscosity data by elimination of the axis ratio l/d. Introduction of formula (4) into (8) and combination with (7) yields the result:

$$\left.\begin{aligned} &D=\text{const } M^{-(\frac{1}{2}+0.454p)};\quad s=\text{const } M^{\frac{1}{2}-0.454p}.\\ &\text{Consequently for } p=1:\\ &\qquad D=\text{const } M^{-0.79},\quad s=\text{const } M^{0.21};\\ &\text{for } p=0:\quad D=\text{const } M^{-\frac{1}{2}},\quad s=\text{const } M^{\frac{1}{2}}. \end{aligned}\right\} \tag{9}$$

The constants are independent of the molecular weight in a given series, having a given p-value.

In the limit of a straight chain, the sedimentation constant becomes almost independent of molecular weight. This is to be expected, since s depends for long chains mainly upon the ratio M/l. If Staudinger's rule holds, $p=0.59$ and

$$D=\text{const } M^{-0.60},\quad s=\text{const } M^{0.40}. \tag{9a}$$

Equation (9) is not strictly applicable to the extreme of an ideal coil ($p=0$), since it is based on relation (7), valid if the molecular volume of the polymer increases with the first power of M. For the average Kuhn-coil, however, it is proportional to $M^{\frac{1}{2}}$, thus causing the diffusion constant to vary with the reciprocal square root of M. The experimental data presented below give exponents in the neighborhood of $\frac{1}{2}$. Their interpretation on such a basis, however, is incompatible with the observed viscosity behavior. Kuhn's recent considerations[10] are not in agreement with (9) and (9a). This arises from the corresponding divergence in the interpretation of Staudinger's rule, pointed out in Part II. A formula of type (9) has been proposed by Gralén,[19] without any relation to viscosity or the degree of internal flexibility of the chain. From his empirical exponents for cellulose, cellulose nitrate in acetone and sodium cellulose xanthate, approximate values of p equal to 0.47, 0.78, 0.41 and of a equal to 0.80, 1.32 and 0.70 are calculated.

For an inhomogenous system, Eq. (9) indicates that no number- or weight-average molecular weight is obtained by forming the ratio

$$\langle s\rangle_{Av}/\langle D\rangle_{Av}.$$

The same holds for measurements of free diffusion or of ultracentrifuge rates. Equation (9) indicates what type of average is to be expected, if the viscosity-molecular weight relation (2) is known for the series. It may be noted that the variations in the dependence of s and D upon M with the nature of the polymer and solvent system are much slighter than in respect to viscosity behavior.

In Table V are presented p-values computed from the observed dependence of s or D upon M (Eq. 9), and are compared with those obtained from viscosity by means of relation (5) or directly from the axis ratios. In Figs. 3 and 4,

TABLE V. Values of flexibility parameter p.

Compound	From diffusion	From sedimentation	From viscosity	Max. dev. %
Methyl cellulose[a]	0.57[b]	—	0.59[c]	5
Cellulose nitrate[d]	—	0.48	0.60	11
Amylose acetate[e]	0.48	0.49	0.53–0.57[f]	11 (sed.)

[a] See reference 2.
[b] See reference 24.
[c] The values for l/d originally given in Table III of reference 1 are erroneous and should be replaced respectively by 38.5, 55.5, 69.5, resulting in the above exponent.
[d] See reference f of Table I.
[e] See reference 22.
[f] The lower value results from a comparison of the axis ratios determined by means of f/f_0 with the molecular weights. The upper one is derived from the viscosity values of l/d and has been used in Fig. 4.

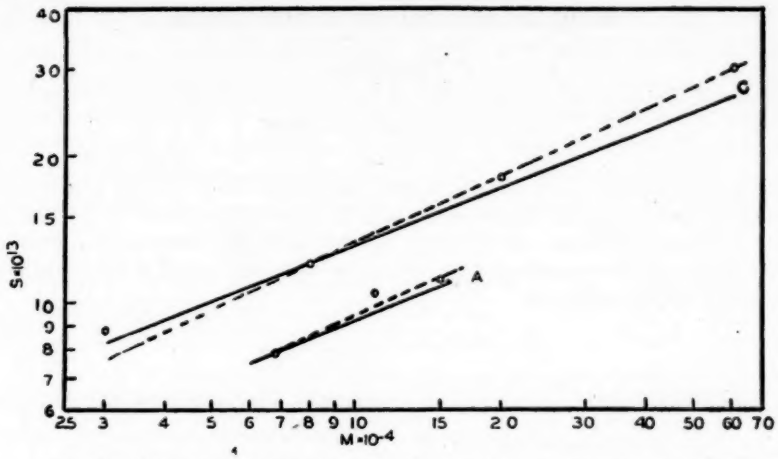

FIG. 4. Double logarithmic plot of sedimentation constants s *vs.* molecular weight M for amylose acetate (A) and cellulose nitrate (C). Circles indicate experimental values, dashed lines experimental slopes, solid lines computed ones.

D or s are plotted *vs.* M for these three polymer systems. For cellulose nitrate, the slope of the line through the second and the last point was calculated; in the other cases the two end points were used. The computed D or s were fitted through the second point in the former case and through the first one otherwise, using the p-values from viscosity in Eq. (9). The extent of the agreement between viscosity data and ultracentrifuge results, as interpreted by the present theory, is shown by a comparison of the slope of the solid lines (the p from viscosity data), and that of the dashed lines (the p from rate data). The last column in the table above contains the maximum deviations between experimental sedimentation or diffusion data and those calculated. In view of the accuracy obtainable and of factors discussed above, it does not appear necessary to determine the slopes in a more accurate manner. The molecular weights used in Figs. 3 and 4 represent ultracentrifuge values. It would be very desirable to have osmotic determinations in addition. The agreement obtained seems satisfactory, in spite of the fact that in two cases only two points were available for determining the slope, as may be judged from the graphs. Attempts to apply this theory to Signer's and Gross'[23] sedimentation data on some polystyrene samples and to Polson's[24] data on cellulose acetate meet with failure, the exponents p turning out to be too small or too large. It would be very desirable to have sedimentation and diffusion data on the polystyrene and cellulose acetate fractions referred to in Table I.

Summarizing, it may be stated that by means of a combination of the present theory[1,10] of intrinsic viscosity of long molecules with certain semi-empirical results on the shape of flexible chains in solution, it is possible to interpret the empirical relation between intrinsic viscosity and average degree of polymerization arising from a modification of Staudinger's rule, and to account for variations in the exponent with the nature of the polymer and of the solvent or solvent mixture.[25] Application of the hydrodynamic theory of sedimentation and diffusion combined with the above results gives the sedimentation or diffusion constant as a function of the molecular weight and the variation of this function with the internal flexibility of the chain and with the medium.

The author wishes to express his appreciation to Dr. John J. Grebe for the interest shown in this work.

Aid in carrying out the numerical calculations was received from Misses M. E. Chaplin and D. R. Simmons.

[23] R. Signer and H. Gross, Helv. Chim. Acta **17**, 348 (1934).
[24] Computed from data by A. Polson, Kolloid Zeits. **83**, 172 (1938).
[25] The influence of such factors on higher terms in the viscosity-concentration relation has since been discussed by E. M. Frith, Trans. Faraday Soc. **41**, 17, 90 (1945).

Analysis of Excitation Functions

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The mechanical laws of impact lead to the conclusion that, in any transfer of kinetic energy into quantized energy (excitation, dissociation), the "excitation function" should, at the threshold, start from zero and increase with increasing kinetic energy. This shape of the function is likely to cause a systematic error in the measurement of critical energies with certain non-equilibrium methods.

I. PROBLEM

THE procedures for the determination of chemical energies, for example, energies of dissociation, may be classified into equilibrium and non-equilibrium methods. Chemical *equilibria* are not affected by probabilities of transition between the various states present, since, in the underlying thermodynamic relations, only *properties of states* are involved (energies, statistical weights), but no *probabilities of transition*. The situation is different for non-equilibrium methods in which the rate of a process is observed as a function of the temperature. The accuracy of such methods is restricted by lack of information regarding probabilities of transition. This will be evident from an example recently discussed by Dwyer and Oldenberg[1] in their comparison of the various methods for the determination of the energy $H_2O \rightarrow H+OH$. We consider the breaking up of H_2O molecules into H+OH by impacts of the second kind with excited mercury atoms. Since the energy of excitation of the mercury atom is slightly deficient, the energy of the thermal collisions provides the balance if the temperature is high enough. Thus the *increase of rate* observed with increasing temperature is attributed to the *increase of the number of thermal collisions* occurring with sufficient energy. In this argument the same effect is attributed to any thermal collision occurring with an energy above the threshold. Hence the argument fails to take into account the possibility that a collision occurring with an energy slightly above the threshold may have an efficiency strongly dependent upon this excess energy. This dependence (efficiency of collisions against excess energy) is called the excitation function of the process. The excitation function must be known for a quantitative, theoretical interpretation of the rate observed as a function of the temperature.

The only process for which excitation functions have been measured is the excitation of atoms by electron impact. In this instance the efficiency of the impact, starting from zero at the threshold, rapidly increases with the excess kinetic energy of the impinging electron.[2]

In order to judge non-equilibrium methods we must find out whether the rapid increase of the excitation function just above the threshold is a special property of the process just mentioned or is expected to apply as well to other processes. A special case which can be analyzed in some detail leads to a general conclusion regarding excitation functions right above the threshold.

II. SPECIAL CASE

As a special case we analyze the excitation of molecular vibration by electron impact. According to Eucken and Franck,[3] the molecule simply picks up vibrational energy, while only very small amounts of linear or angular momentum can be transferred because of the ratio of masses of electron and molecule.

The "controlled electron impact experiment" deals with impacts in which a fast electron hits an atom or molecule which is at rest with respect to the observer. Such impacts fail to cause quantum transitions if the kinetic energy W has

[1] R. J. Dwyer and O. Oldenberg, J. Chem. Phys. **12**, 353 (1944). See O. Riechemeier, H. Senftleben, and H. Pastorff, Ann. d. Physik **19**, 202 (1934).

[2] W. Hanle and K. Larché, Ergeb. d. exakt. Naturwiss. **10**, 285 (1931).

[3] J. Franck and A. Eucken, Zeits. f. physik. Chemie **B20**, 460 (1933).

merely the value Q of the energy of excitation computed from spectroscopic data. This failure is due to the fact that, according to the laws of conservation, the common center of gravity of the system continues its path after the impact so that the kinetic energy of the impinging particle is not fully available for the quantized process. In the impact most favorable for excitation, that is the central impact, W must at least equal $Q(M+m)/M$. (M and m = masses of atom and impinging particle, respectively.)[4]

For excitation by impact of *electrons* the factor $(M+m)/M$ is nearly unity, so that no *noticeable* excess of the kinetic energy W over the excitation energy Q is needed *for the central impact.* We are interested, however, in another aspect of the impact. For off-center impacts the electron will bounce off obliquely and retain a larger part of its initial energy. Therefore, in this case, only an electron with higher kinetic energy W will be able to produce excitation. *Vice versa*, a faster electron has a greater chance for being effective because it can act anywhere within a larger central part of the cross section of the target atom. Thus we can correlate the kinetic energy of the impinging electron with the probability of excitation. That is, we can make a prediction regarding the excitation function. This function must start from zero because, for the electrons which have exactly the threshold energy, the effective cross section is vanishing.[5]

We do not claim that this kinetic theory furnishes a complete explanation of the excitation function. Instead, the complete representation will consist of two factors, the *kinetic factor* discussed here and a *structure factor*, which is not accessible to a mechanical treatment.

Let us consider an electron incident on the spherical surface of the molecule with the kinetic energy W under an angle α (Fig. 1). It bounces off under another angle, delivering the quantized energy Q. The computation of this process is based on the laws of conservation. The equations so obtained, which may here be omitted, have real solutions only if $\cos^2\alpha \geqq Q/W$, that is, if the kinetic energy of the electron associated with the normal component of the velocity is equal to or larger than Q. Thus, for a given kinetic energy W of the electron, it is possible to compute a limiting value of the angle of incidence α and, hence, the central section πr^2 (see Fig. 1) of the target molecule within which the electron of the energy W possibly is effective. This section divided by the total area πR^2 of the target represents the effective fraction of the target, that is, the kinetic factor k of the excitation function. The result is

$$k=1-Q/W \quad [\text{for } W\geqq Q].$$

As expected, this simple function represents a curve starting from zero at $W=Q$, approaching unity for large W.

The same computation carried through for the case of comparable masses m and M leads to the more general equation

$$k=1-\frac{Q}{W}\left(\frac{M+m}{M}\right) \quad \left[\text{for } W\geqq Q\left(\frac{M+m}{M}\right)\right].$$

In these computations the molecule has been represented as a sphere with a hard surface. But the theory should apply as well to a molecule the force around which is described by a power law. Therefore, it should be possible to derive the same results from the complicated formulas representing excitation functions right above the threshold which have been derived from wave mechanics by Morse and Stueckelberg.[6]

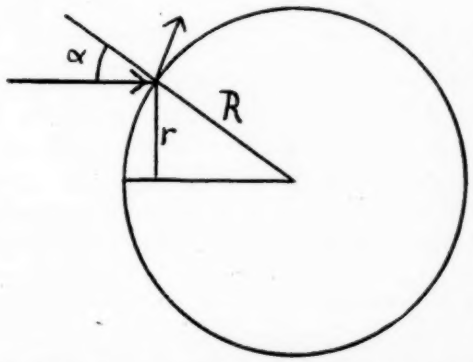

FIG. 1. The arrows indicate the directions of the electron impinging on and bouncing back from the molecule represented by the circle.

[4] On the basis of this restriction G. Joos and H. Kulenkampff computed the minimum kinetic energy of *positive ions* required for the excitation of atoms by impact (Physik. Zeits. **25**, 257 (1924)). Qualitatively, this restriction was discussed by J. Franck (Zeits. f. Physik **25**, 312 (1924)).

[5] This follows from the equations from which Klein and Rosseland concluded the occurrence of impacts of the second kind (Zeits. f. Physik **4**, 49 (1929)).

[6] P. M. Morse and E. C. G. Stueckelberg, Ann. d. Physik **9**, 579 (1931).

A quantitative comparison of the steepness of this theoretical curve with the steepness of the experimental curves[2] is meaningless. The reason is that the experimental curves give only *relative* intensities of spectral lines, hence relative probabilities of excitation. Thus their vertical scales have no absolute significance. We are only interested in the fact that the start of the function from zero follows from the mechanical laws of impact.

III. GENERAL CASE

The principal new aspect of the present argument is the suggestion that the same conclusion be applied to any collision of the first or second kind in which kinetic energy is used to supplement quantized energy. No quantitative statement can be expected, since the above computation is oversimplified by disregarding transfer of angular momentum (assuming excitation of vibration only). Nevertheless, it is plausible to assume that in any such case the *central* collision will be effective with a *minimum* of excess kinetic energy of the partners. This preferred part played by central collisions is due to the fact that, at any off-center collision, a larger part of the kinetic energy must be preserved in translation or rotation. This is another way of saying that the excitation function of any process, as well as of the simple process discussed above, starts from zero at the threshold and increases with increasing relative kinetic energy.

(It is true that this effect of the *kinetic* factor could be counteracted by the *structure* factor. This, however, seems to necessitate very artificial assumptions. For example, it may happen that the *effective* impacts are confined to narrow limits near the direction toward the center. This restriction would eliminate the off-center collisions completely and permit any shape of the excitation function. We disregard assumptions of this type.)

From the steep start of the excitation function we infer that it is unsafe to assume a *uniform* probability of transition above the threshold, as was implied, for example, in the measurement of the energy of dissociation of H_2O discussed in Section I. The practical conclusion is that non-equilibrium methods, although by no means useless, are subject to a systematic error which cannot be quantitatively estimated. Equilibrium methods, on the other hand, are free from this error, since a low probability of transition does not affect the equilibrium except by retarding the rate at which it is reached.